CHEMICAL BONDING

&

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HAND MADE NOTES

07/July/2014

Chemical Bonding

1) Classical Application
   Singlet theory
   Overlapping
   Hybridization
   Shapes of molecules
   VSPER

   [V.B.T.]

2) Dipole Moment
   H-bonding
   VWF
   Metallic Bonding

3) Ionic Bonding
   Polarization
   Lattice energy

4) MOT

5) Back donation

1)

Bond is not a SST, It is only force of attraction b/w two atoms.

What is Bond?

Bond is nothing, but it is a force of attraction b/w 2 atoms or more than 2 atoms.

Parent Bond - Valent Bond.

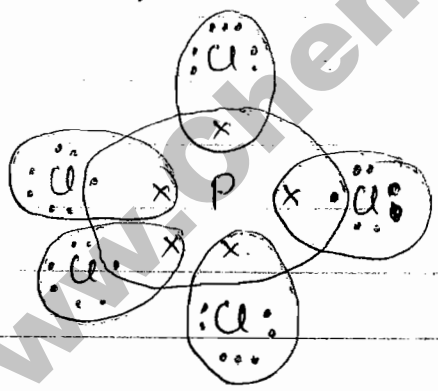
Octate theory given by Lewis & Langumeir

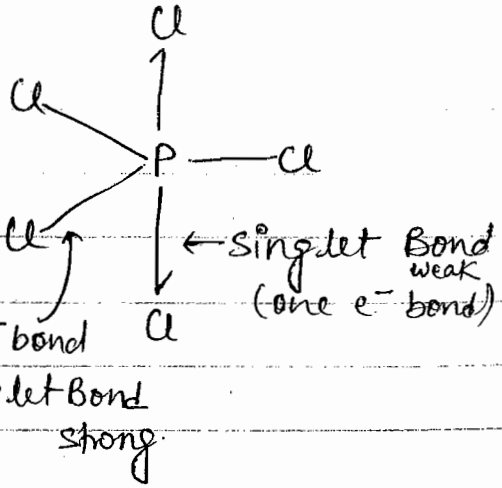
BF_3, BCl_3, $AlCl_3$, ... e^- deficient but stable (Hypovalent) } Octant Rule not follows.

PCl_5, SF_6, SF_4, BrF_5, IF_7 e^- efficient (Hypervalent) } Octant Rule not follows.

Singlet Theory :- by Sugden.

PCl_5





Acc. to theory 2 bond weak i.e. Why - on heating 2 bond breaks.

$$PCl_5 \xrightarrow{\Delta} Cl_2 + PCl_3$$

Q. Find out no. of singlet linkage in.

↳ Bonds more than valency

BF_3 — 0
SF_2 — 0
SF_4 — 2
SF_6 — 4
BrF_5 — 4
$TeBr_4$ — 2
IF_7 — 6
PCl_5 — 2

Sidgwick Theory / Rule of Maximum Valency:-

"An atoms can have more than 8 e^-, they can expand their octant." For the expansion, Atom should have suitable orb.

P = [Ne] $\underset{3s}{\boxed{\uparrow\downarrow}}$ $\underset{3p}{\boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow}}$

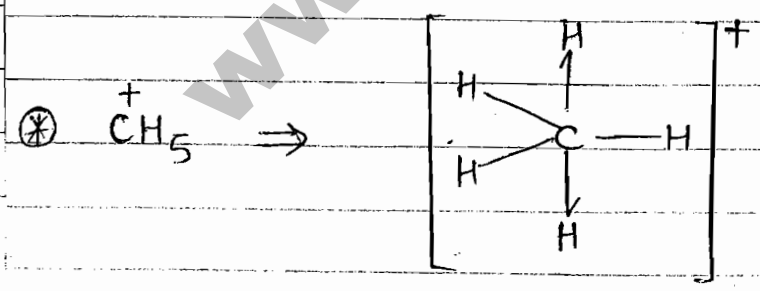
PH_3, PCl_3

$\overset{*}{P}$ = [Ne] $\underset{3s}{\boxed{\uparrow}}$ $\underset{3p}{\boxed{\uparrow}}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\underset{3d}{\boxed{\uparrow}}$ ___ ___

PCl_5, PF_5, PBr_3 ⇒ sp^3d hyb. ✗

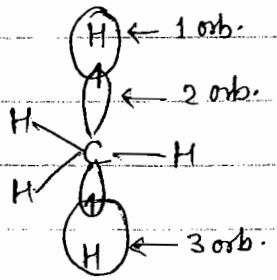
$sp^2 + dp$ hyb. ✓

Atom	Possible Bonding state/Co-ordination No.
H	1
Be	2 $(BeCl_2)$, 3 $(BeF_3)^-$, 4 $(BeF_4)^{--}$, $Be(OH)_4^-$
B	3 (BF_3), 4 $(BF_4)^-$, BH_4^-
Al	3 $(AlCl_3)$, 4 AlF_4^-, 5, 6 $[Al(H_2O)_6]^{3+}$
C	3 $(C\equiv O)$, 4 (CH_4), 5 $(\overset{+}{C}H_5)$, $Fe_5C(CO)_{15}$ 6, $(Fe_6-C(CO)_{18}$
Si	4 (SiH_4), 5, 6
N	3 (NH_3), 4 $(\overset{+}{N}H_4)$, 5 $(\overset{+}{N}D_5)$
P	3, (PH_3), 4, $(\overset{+}{P}H_4)$, 5 (PCl_5), 6 $(\bar{P}F_6)$
F	1
Cl, Br, I ↓ IF_8^-	1, 3, 5, 7



TBP

Hyb. sp^2



3c-2e⁻ bond.

Q. Possible orb. in N -

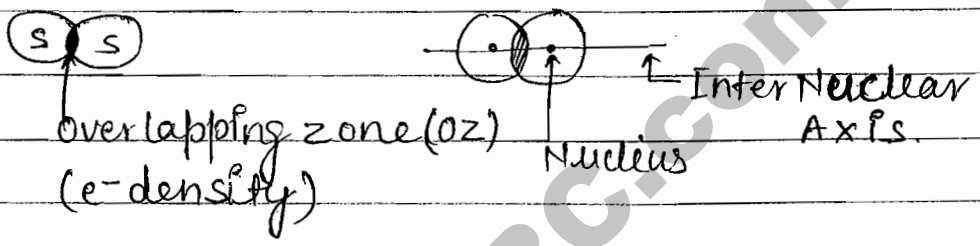
a) 3d b) 4d c) 3p d) all are possible ✓

* In all the atoms all orbitals are possible.

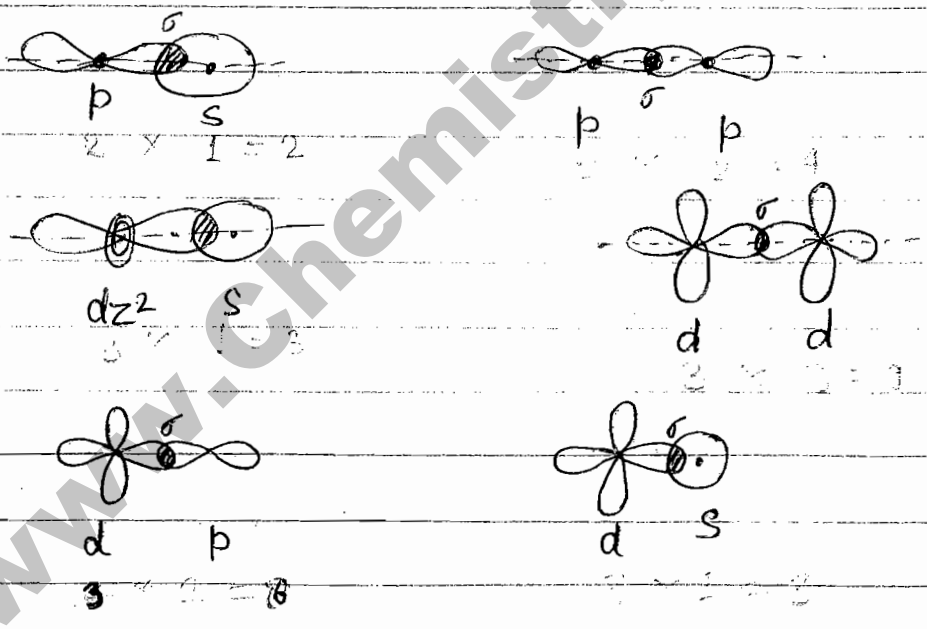
✱All atoms have infinite shells.

Overlapping :

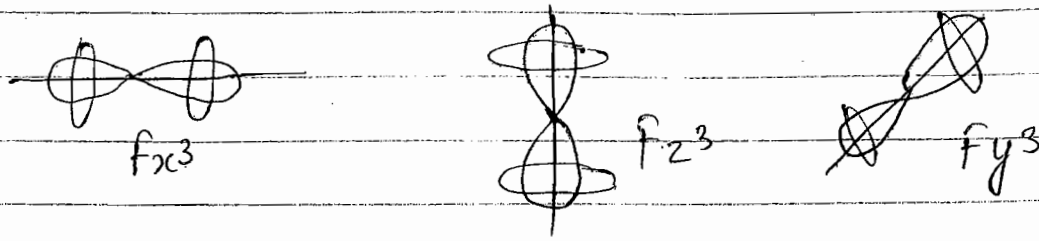
1) Head on or Endwise → σ bond.



Overlapping zone ∝ Strength of bond.



f. orb.



Q. Arrange the strength of bond among s-s, p-p, d-d.

Ans. $s\text{-}s < p\text{-}p < d\text{-}d$

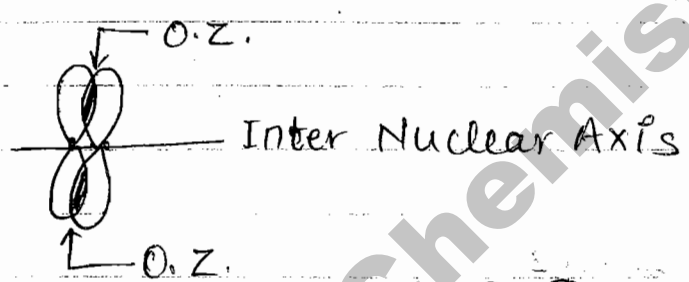
Strength order →

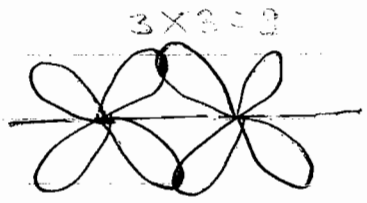
Overlapping zone increase →

2) Sidewise or Parellel or Lateral Overlapping.

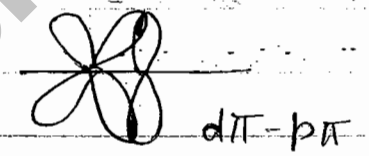
Found, where unhybridised orb. present.

* π -bond formed by unhybridised orb.





$d\pi - d\pi$

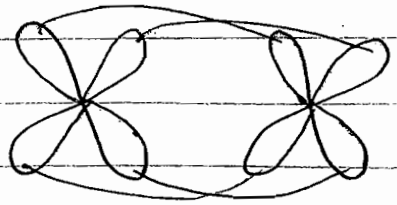


$d\pi - p\pi$

Two overlapping zone in π - bond.

* For strong bond overlapping zone should be on Inter Nuclear Axis. On the basis of this
* σ bond is stronger than π - bond.

3) Facewise Overlapping (δ - Bonding)



δ - bonding
(4-overlapping zone)

—	=	≡	≡ (π, π, δ)
Single Bond. ①	double ②	Tripple ③	quadruple bond. ④

④ & ⑤ are super short Bonds

≡ (δ, π, δ, π, δ) ⑤
quintet bond.
quintuple bond.

$[ArCr \equiv CrAr]^{n\pm}$ ← g.

discovered in 2007.

* Phi bonding
* Gamma bonding

} are possible in future

Note: π^* antibonding orbital have similar of overlapping like that δ (Delta)

$p\pi - p\pi$ bonding

$2p\pi - 2p\pi$ ← found in Second Period (Be, B, C, N, O)

$3p\pi - 3p\pi$ ← found in IIIrd Period (Al, Si, P, S)

$4p\pi - 4p\pi$

$5p\pi - 5p\pi$

Strength ↓

* $2p\pi - 2p\pi$ somewhere strong i.e. why atoms formed $2p\pi - 2p\pi$ bond where as $3p\pi - 3p\pi$ is weak i.e. why atoms does not form.

eg. $N \equiv N$ $\quad$ $O = O$

$2p\pi - 2p\pi$ $\quad$ $2p\pi - 2p\pi$

$P \equiv P$ $\quad$ $S = S$

✗ $3p\pi - 3p\pi$ $\quad$ ✗ $3p\pi - 3p\pi$

C → Diamond (σ bonding)
→ Graphite (π bond)
→ Fullerene (π-bond)

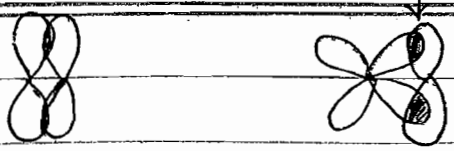
Si → Diamond (σ bond)
→ Graph ✗
→ Fullerene ✗

Q Arrange the stability of bonding among $3p\pi - 3p\pi$, $3d\pi - 3p\pi$, $3d\pi - 2p\pi$

Ans. $3d\pi - 2p\pi > 3d\pi - 3p\pi > 3p\pi - 3p\pi$

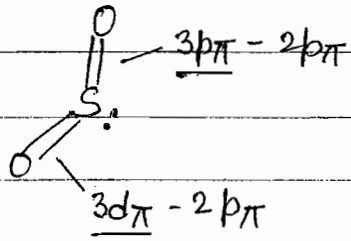
↑ small orb. will approach more for bonding

Inclinde nature (More overlapping).

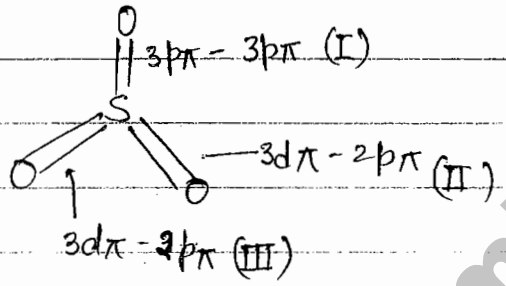


$3p\pi - 3p\pi$ Weak Bond.

$3d\pi - 3p\pi$ Strong bonding

Q 

stability ? $3d\pi - 2p\pi > 3p\pi - 2p\pi$

Q 

stability order.

a) I = II = III

b) I > II > III

c) I > II ≡ III

d) I < II ≡ III

Ans: All bonds are equally stable due to resonance.

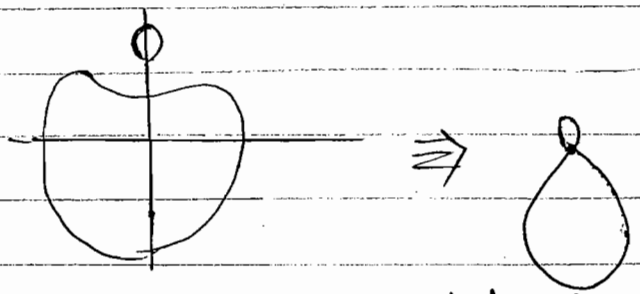
I.U.PAC ⇒ Eye-u-pac

Nomenclature आई यू पैक

Ist Nobel Award to Lebel in 1901 for discovary of shape of CH_4

CONCEPT of HYBRIDISATION

$H_2\ddot{O}$ ⇒ sp^4 hybridisation. , $\ddot{N}H_3$ ⇒ $sp^{3.5}$



Bond Angle ∝ s character

Hybrid orbitals (Non Real)

sp^3	109°	25%	75%	Less s% i.e. why less spherical
sp^2	120°	33.3%	66.6%	
sp	180°	50%	50%	more s% i.e. why more spherical

* Hyb. orb never form π-bond because they can't overlap partially.

can't overlap

$$\cos\theta = \frac{S}{S-1}$$

↑ Bond Angle

* As the bond angle increases, p-character decreases. and vise-versa.

Note: In H_2O bond angle 104° instead of 109°28' that means angle decrease hence p-character will increase & hence p% = 80% Now s% will be 20% ⇒ sp^4 hyb.

Prafull chandra Roy father of Indian chemistry

s% of orb $\propto \frac{1}{\text{Energy}}$

Concept of Hybridisation :- by Pauling.

"Process to mix and redistribute Energy to diff. orb. to make them identical in shape, Energy & angle"

Criteria :-

i) Newly form orb. are called Hyb. Orb. (H.O.)

ii) Hyb. is hypothetical phenomenon hence H.O. are non real.

iii) At the time of hyb. the redestribution of energy takes place. therefore H.O. at the time of their birth have similar energy, shape & angle.

iv) Hyb. orbitals always forms σ bond., the shape of hyb. orb. depends upon the % character of orb. specially s-character. As the s-character increases, the electronegativity increases therefore energy of hyb. orb. decreases.

v) % character also depends upon angle b/w hyb. orb. greater the angle, more will be s-character.

$$\cos\theta = \frac{s}{s-1} = \frac{p-1}{p}$$

Just a mathematical Approach

Types of Hybridisation :-

Steric No.(s) = No. of l.p. + no. of b.p.

= No. of l.p. + no. of σ-bond.

H—Cl doumbled shape

All mol. having 2 atoms ⊥

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Main Group Element :- One shell incomplete Eg. Na, Cl, (Zn)

Transition Metal " :- More than 1 shell " Eg. Fe, Co, - - - -

Noble gas " :- All shell complete Eg Ne, He, Ar - - -

C.N. / S.N. / Hyb Orb No.	Geometry	Hyb.	Bondangle	Eg
2	Linear	sp	180	Cl—Be—Cl (180°)
3	Trigonal	sp^2	120°	BH_3
3	Trigonal pyramidal		90°	VO_2^+
4	Tetrahedral	sp^3	109°	CH_4
4	Tetrahedral	sd^3/d^3s		$KMnO_4$, $K_2Cr_2O_4$, CrO_2Cl_2
4	Sq. planar	dsp^2	90°	$[Ni(CN)_4]^{2-}$
4	Sq. planar	sp^2d	90°	$[Cu(NH_3)_4]^{++}$
5	T.B.P.	$sp^2 + pd_{z^2}$	120°, 90°	PCl_5
5	Sq. pyramidal	sp^3d	90°	

Main Group Element always form Outer orb. comp

Main " " 99% Forms Td. Geometry on C.N. 4

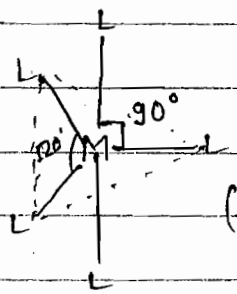
Transition " " Td as well as Sq. planar on C.N. 4

Q Which hyb. don't follow criteria of hyb.

a) sp (180°) b) sp^2 (120°) c) sp^3 (109°) d) sp^3d (120°+90°) e) sp^2d (90°) f) sp^3d^2 (90°)

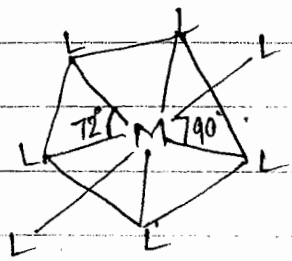
g) sp^3d^3 (72°+90°)

Hyb. orb. ⇒ same energy, shape & (Angle)



All the bond angles are not equal hence this hyb. discard criteria of hybridisation

(sp^3d ⇒ TB.P.)



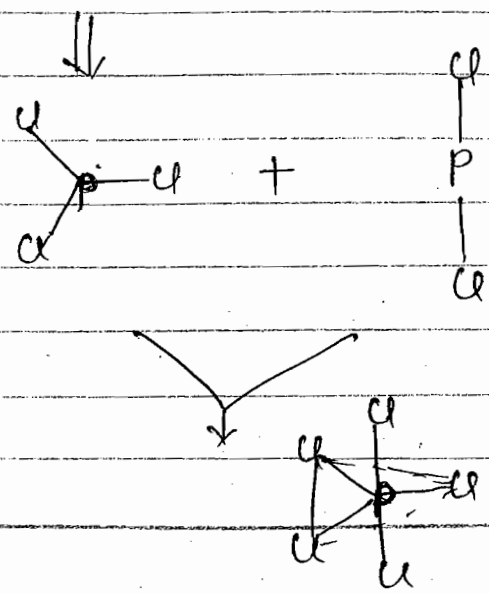
All the bond angles are unequal in sp^3d^3 hyb. hence it does not follow the criteria of hybridisation.

* PCl_5

1	1	1	1	1	—	—	—	—
3s	$3p_x$	$3p_y$	$3p_z$	d_{z^2}				

sp^2 ⇒ 120° p-d ⇒ 180°

In PCl_5 there are two bond angles in geometry i.e. 120° & 90+90=180° These angles are possible by sp^2 & p-d hyb.



$[VO(acac)_2]$ Geometry ⇒ Sq. py.

Main Group Element (M.G.E).

- TBP ⇒ Usually 2, 3 period element forms. TBP.
- Sq.py. ⇒ Usually 5, 6 " " " Sq. py.

Transition Metal Element (T.M.E.)

- TBP. ⇒ 3d usually forms. TBP.
- Sq. py ⇒ 4d, 5d usually forms. Sq. py str.

* As We go top to bottom in a group. tendency of forming sq. py. increases.

NET 2014

$P Ph_5$ → TBP
$As Ph_5$ → TBP
$Sb. Ph_5$ → Sq. py.

* Geometry:- Decides by ~~q~~ hybridisations. Means l.p. included.

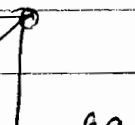
* Shape/Structure: l.p. does not included in shape

Eg. $\ddot{N}H_3$ → Td geometry & Shape Pyramidal
$H_2\ddot{O}$ → " " & Shape V-type

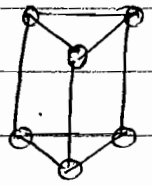
Perfect Td, Oh, Icosahedral str. are Spherical Structure

dx^2y^2 dz^2 dz^2

S.N.(6) → Oh sp^3d^2 / d^2sp^3
↳ Sq. bi pyramidal.

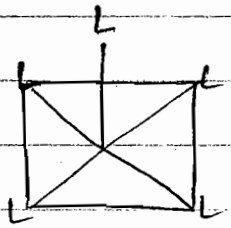


→ Pentahedron. sd^5
(or) Trigonal prismatic



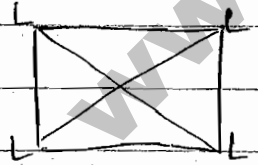
eg. $[TaF_6]^{4-}$, WMe_6

Capping & Decapping Rule.



Monodecapped Oh.
NIDO

−L



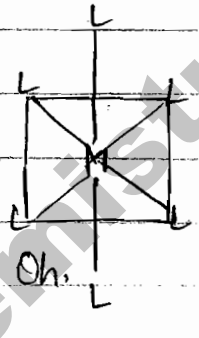
Bidecapped Oh or Sq planar.
ARACHNO

−L

HYPO

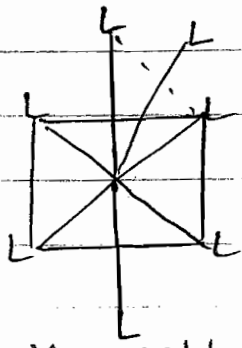
−L → KLADO

Decapping
−L



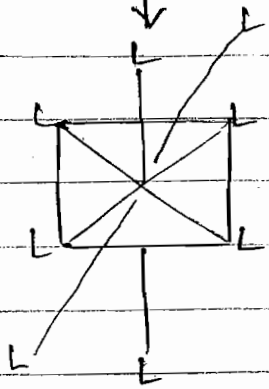
Oh.
CLOSO

Capping
+L



Monocapped Oh.
HYPER

+L



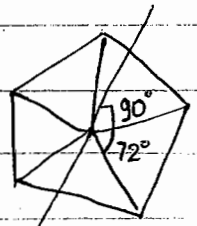
Bi capped Oh
SUPER CLOSO

+L → SUPER SUPER CLOSO

S.N.(7) → Pentagonal bi pyramidal

Hyb. sp^3d^3

Eg IF_7

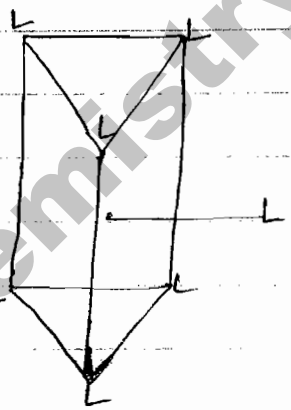


All bond angles are not equal i.e. why sp^3d^3 hyb. is wrong

dyz, dzx, dz^2 participate in hyb. but dxy & dx^2y^2 not

S.N.(7) → Monocapped Trigonal ~~pyramidal~~ prismatic

Eg. TaF_7

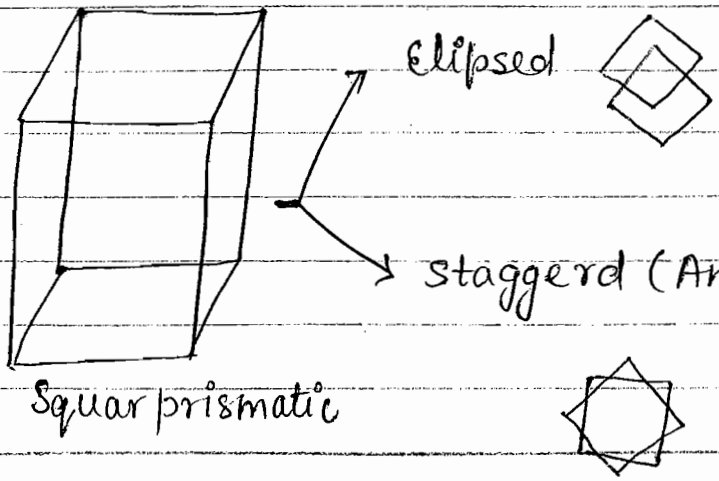


hyb. sp^3d^3

dyz, dzx, dz^2 participate in hyb. but dxy & dx^2y^2 not.

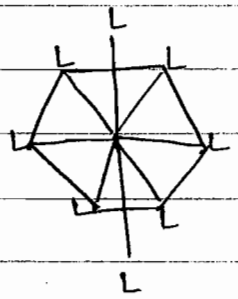
S.N.(8) → Square antiprismatic Eg. $IF_8^{\ominus}$

hyb. sp^3d^4



S.N. (8) - Eg. $Mo(CN)_8^{2-}$ hyb. sp^3d^3f cubic str.

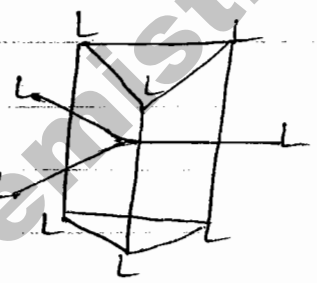
S.N. (8) → Hyb. sp^3d^4



Dodecahedron.

dxy, dyz, dzx & dz^2 take part in Hyb.

S.N(9) Eg. $[ReH_9]^{3-}$ hyb. sp^3d^5



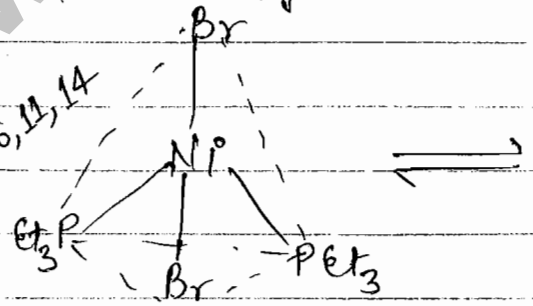
Tricapped, Trigonal Prismatic

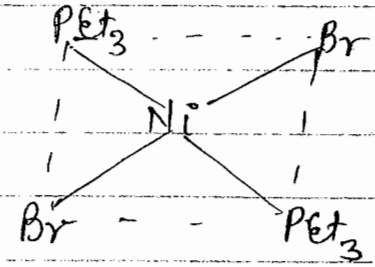
Note: Hyb. of any molecule decided by the geometry of molecule.

Polytopal Allagonal Isomerism

?

NET 2004, 06, 11, 14





Td. str. Sq. planar str.

Some times two geometries of same S.N. exist togather in crystal because they have very low energy barriers, this isomerism of a molecule to exist in two geometry, is called Polytopal Allagonal Isomerism.

Determination of Hybridisation

$$H = \frac{1}{2}[V + M - C + A]$$

Valid for M.G.E.

H = No. of hyb. orb.

2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2
7	sp^3d^3
8	sp^3d^4
9	sp^3d^5

C = Charge on cation

A = " " Anion

V = Valence Electron in Central atom (C.A.)

M = No. of <u>mono valent atoms</u> or groups attached with central atom through single bond.

<u>Central Atom</u>

* Less in no.
* Big in size
* More valence state

Eg. SF_4 $\quad H = \frac{1}{2}[V + M - C + A]$

$H = \frac{1}{2}[6 + 4 - 0 + 0]$

$H = 5 \Rightarrow sp^3d$

SF_6 $\quad H = \frac{1}{2}[6 + 6 - 0 + 0]$

$H = 6 \Rightarrow sp^3d^2$

$COCl_2$ $\quad H = \frac{1}{2}[4 + 2]$

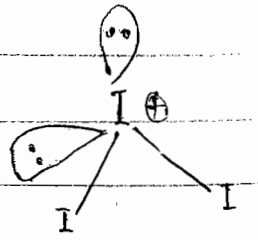
$H = 3 \Rightarrow sp^2$

SO_3^{2-} $\quad H = \frac{1}{2}[6 + 2]$

$H = 4 \Rightarrow sp^3$

I_3^+ $\quad H = \frac{1}{2}[7 + 2 - 1 + 0]$

$H = 4 \Rightarrow sp^3$



H_2SO_4 $\quad H = \frac{1}{2}[6 + 2 - 0 + 0]$

$H = 4 \Rightarrow sp^3 / dsp^2$

SO_3 $H = \frac{1}{2}[6+0-0+0]$

$H = 3 \Rightarrow sp^2$

CO $H = \frac{1}{2}[4+0-0+0]$

$H = 2 \Rightarrow sp$

CO_2 $H = \frac{1}{2}[4+0-0+0] = 2$

$\Rightarrow sp$

$SnCl_2$ $H = \frac{1}{2}[4+2-0+0]$

$H = 3 \Rightarrow sp^2$

CCl_4 $H = \frac{1}{2}[4+4-0+0]$

$H = 4 \Rightarrow sp^3$

HS^- $H = \frac{1}{2}[6+1-0+1]$

$H = 4 \Rightarrow sp^3$

$SOCl_2$ $H = \frac{1}{2}[6+2+0+0]$

$H = 4$ sp^3

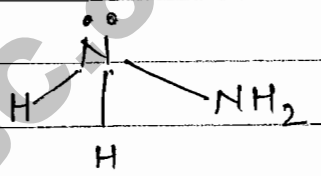
SO_2Cl_2 $\quad H = \frac{1}{2}(6+2-0+0)$

$H = 4 \Rightarrow sp^3$

CH_3Cl $\quad H = \frac{1}{2}(4+4-0+0)$

$H = 4 \Rightarrow sp^3$

N_2H_4 $\quad H = \frac{1}{2}(5+3-0+0)$



$H = 4 \Rightarrow sp^3$

XeO_2 $\quad H = \frac{1}{2}(8+0-0+0)$

$H = 4 \Rightarrow sp^3$

XeO_3 $\quad H = \frac{1}{2}(8+0-0+0)$

$H = 4 \Rightarrow sp^3$

XeO_4 $\quad H = \frac{1}{2}(8+0-0+0)$

$H = 4 \Rightarrow sp^3$

XeF_2 $\quad H = \frac{1}{2}(8+2-0+0)$

$H = 5 \Rightarrow sp^3d$

XeO_2F_2 $H = \frac{1}{2}(8+2-0+0)$

$H = 5 \Rightarrow sp^3d$.

PO_4^{-3} $H = \frac{1}{2}(5+0-0+3)$

$H = 4 \Rightarrow sp^3$

Tetrahedral str.

PCl_6^- $H = \frac{1}{2}(5+6-0+1)$

$H = 6 \Rightarrow sp^3d^2$

PCl_4^+ $H = \frac{1}{2}(5+4+0-1)$

$H = 4 \Rightarrow sp^3$

$H_2PO_4^-$ $H = \frac{1}{2}(5+2+1)$

$H = 4 \Rightarrow sp^3$

BrF_5 $H = \frac{1}{2}(7+5-0+0)$

$H = 6 \Rightarrow sp^3d^2$

IF_7 $H = \frac{1}{2}(7+7-0+0)$

$H = 7 \Rightarrow sp^3d^3$

BrI_3 $H = \frac{1}{2}(7+3-0+0)$

$H = 5 \Rightarrow sp^3d$

S.N. = Stearic No.

09/July/2014 22

VALENCE SHELL ELECTRON PAIR REPULSION MODEL

(VSEPR MODEL)

* Model is based upon repulsions among e⁻ pair (lp or bp).

* It gives an idea about str & shape of molecule.

* The str. of molecule is that in which the repulsions among e⁻ pair is minimum, i.e. max stable. eg CH_4 is Td becoz in this situation it have min. repulsion.

* The repulsion follows the order lp-lp > lp-bp > bp-bp.

e⁻ pair

- l.p. — Influence of single atom.
- b.p. — Attracted by two nuclei

Postulates:-

*

	CH_4	$\ddot{N}H_3$	$H_2\ddot{O}$
bp	4	3	2
lp	0	1	2
S.N.	4	4	4
Geometry	Td	Td	Td
Shape	Td	Trigonal py.	V-shape (Bent)
Angle	109°	~107° (Almost.)	~105°

C.A. ⇒ Central Atom

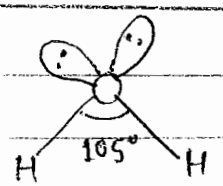
* If central atom has no l.p. having only b.p. then the shape is same as the geometry, i.e no distortion in bond angle.

* If C.A. has both lp & bp. then due to repulsion bond angle change & distortion take place i.e. shape & geometry are different.

Q. H_2O has an angle of 105°. the repulsion follows the order.

a) lp-lp = lp-bp = bp-bp.

b) lp-lp < lp-bb < bp-bp



Ans. H_2O; bond angle 105° ⇒ All bonds feels min. repulsion at 105° i.e. why all bonds are equally stable.

* If the electro-vity (χ) of C.A. decreases (size increases) then bond angle decreases.

NH_3

PH_3

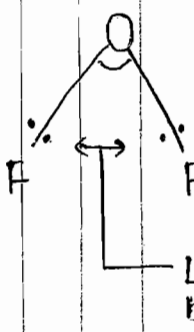
AsH_3

SbH_3

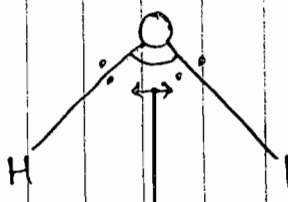
BiH_3

χ and bond angle decreasing on top to bottom.

* If the electronegativity (χ) of surrounding atoms decreases then bond angle increases.

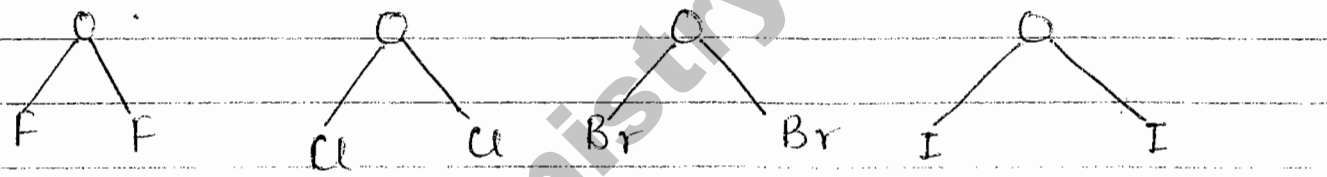


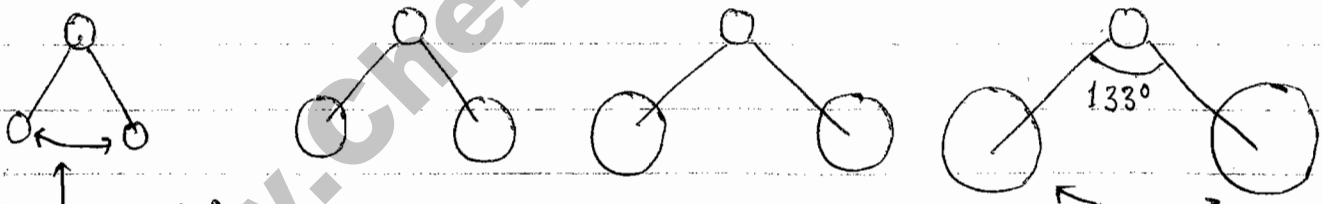
Less Repulsion b/w b.p - b.p (Bond angle Less)



More Repulsion b/w b.p - b.p. (Bond angle Big)

* If size of surrounding atom increases, steric repulsion increases and bond angle increases.

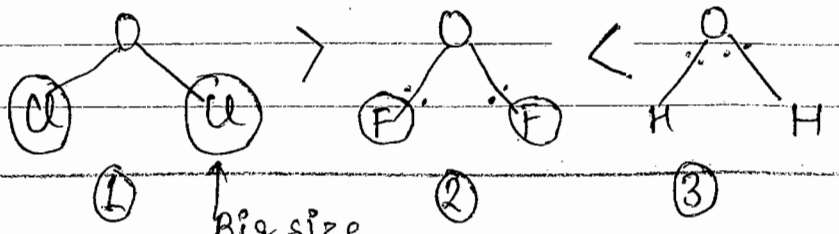




less repulsion due to small size of 'F' i.e. why angle small.

more repulsion due to big size of I i.e. why Angle increased

Q Arrange the bond angle OH_2, OF_2, OCl_2

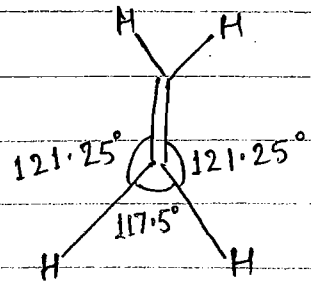


Order of Bond Angle ① > ③ > ②

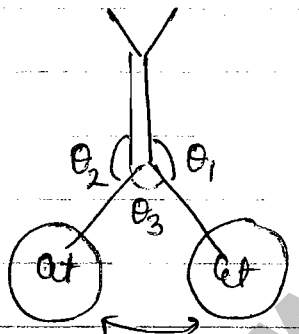
imp

$NCl_3 > NH_3 > NF_3$	$SCl_2 > SH_2 > SF_2$
$AsCl_3 > AsF_3 > AsH_3$	$SeCl_2 > SeF_2 > SeH_2$

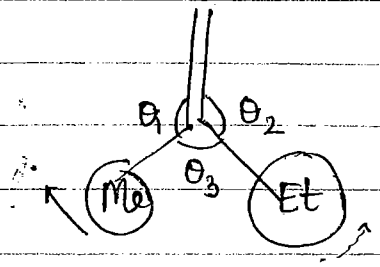
* π-e^- are loosely bonded therefore they can act as l.p. and shows more repulsion with bp.



Ethylene ⇒ Works as base due to π clewd.

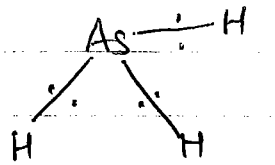


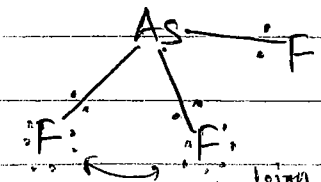
$\theta_1 = \theta_2 < \theta_3$

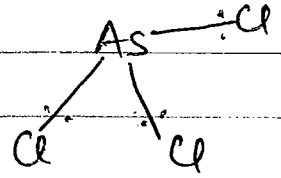


$\theta_3 > \theta_2 > \theta_1$

'As' is not very much ↗ atom hence e^- of As–H bond lies b/w both atoms.







Bond angle ↓ in ACl_3 Biggest due to big size of Cl. Bond angle $AsF_3 > AsH_3$ due to more bp-bp hind. in AsF_3 ↗

* Some times back-donation takes place due to which bond angle changes.

SHAPE OF MOLECULE

Steps :-

* Find S.N.
* Find Geomerty
* Mind Minimum Repulsion condition
* Don't consider lp. in shape.

S.N. 5

Geometry T.B.P.

Eg. PCl_5, PF_5 → No. lp.

hence. Geo. = Shape.

T B·P = T B P.

$I_3^{\oplus}$

bp. = 2, lp = 2

S.N. = 4

Geometry ⇒ Td.

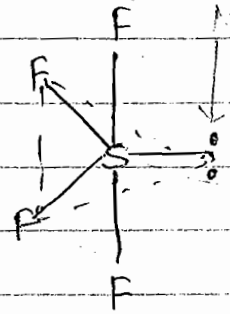
Eg SF_4

bp. = 4 lp. = 1

lp. - lp. } Never

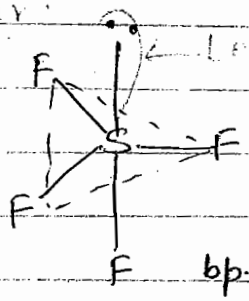
lp. - bp. } want to be at 90°

If we show angle 90° then str is unstable.



lp. - bp. = 90° ⇒ 2

✓



bp. - lp. = 90° ⇒ 3

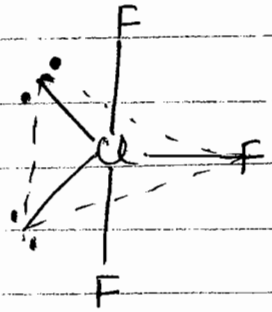
✗

Note. lp should be on equatorial position

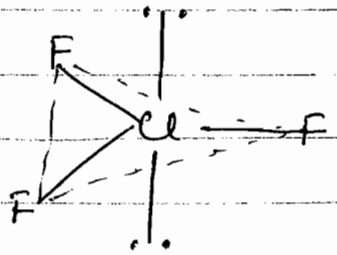
$\top \Rightarrow$ Sea saw str.

Eg ClF_3

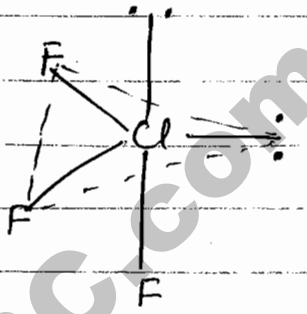
3 bp + 2 lp.



lp. bp. = 90° ⇒ 4 ✓



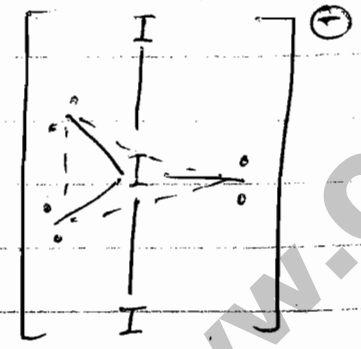
l.p. bp = 90° = 6

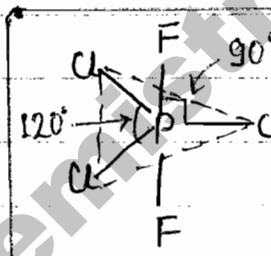


lp. lp. = 90°

Most unstable

Eg. $I\overset{\ominus}{F}_2$, $I_3^{\ominus}$, $I\overset{\ominus}{Cl}_2$



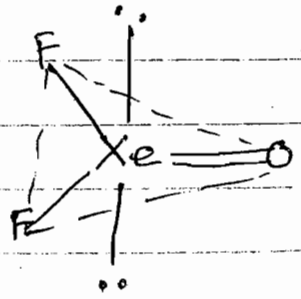


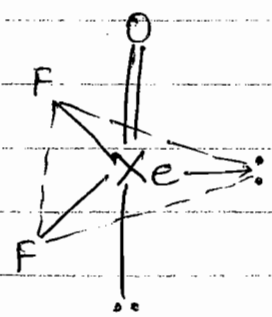
More bond angle ⇒ more s-character that is more near to nucleus means more electronegativity.

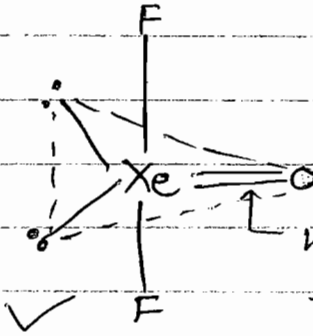
Now it is clear that orb. on more bond angle side having more π hence more π atom will not form bond from this side i.e. F (more π atom forms bond from less π -side i.e. axial side.

Eg. $XeOF_2$

lp. = 2 , bp = 3





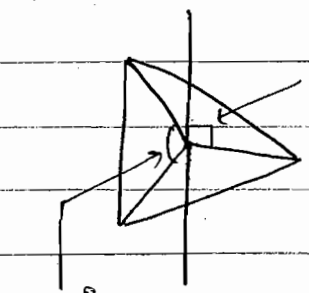


Working as lp.

✓

BENT RULE

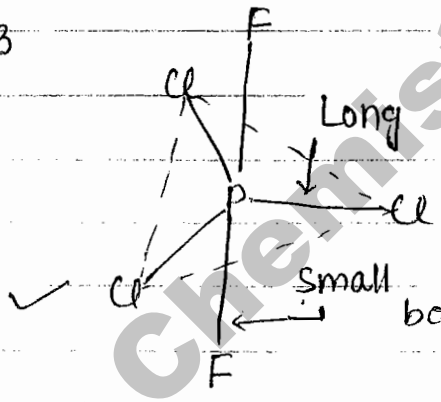
In TBP str. the more electronegative group prefers <u>axial</u> position. (only in TBP)



less angle ⇒ ~~more~~ less s-character ⇒ χ less

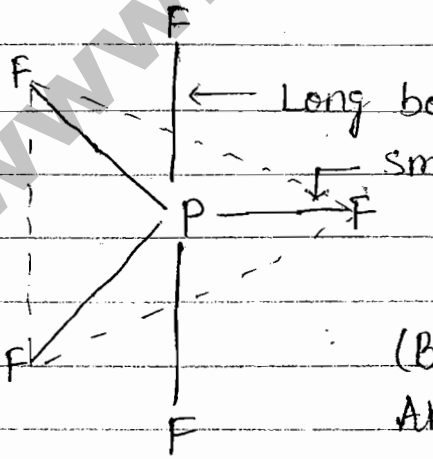
more angle ⇒ More s-character ⇒ χ More

Eg. PF_2Cl_3



bond length (equatorial) due to big size of Cl

bond length (axial) due to small size of F



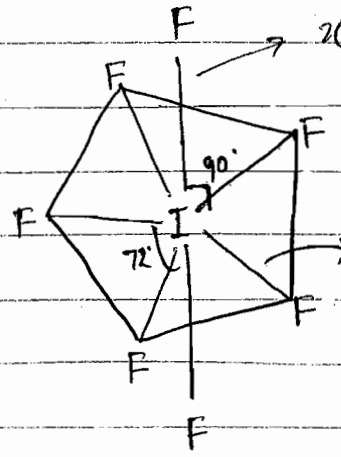
← Long bond at Low temp. (Axial)

Small bond at low temp. (Equatorial)

All bond lengths are equal at room temp. due to fluxional (Berry pseudo rotation) Behaviour. And one F-NMR signal

At low temp. all Bond lengths are not equal. F-NMR signal ⇒ 2.

*



F → χ more (θ = 90°)

↳ Big angle ⇒ More χ

χ less (θ = 72°) ←

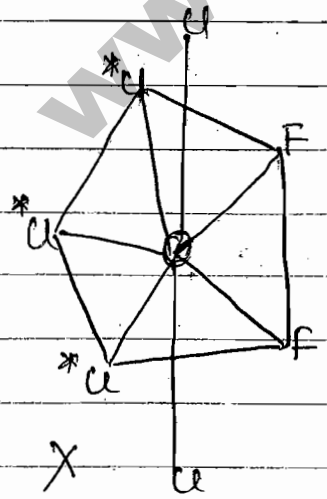
↳ Small angle ⇒ Less χ

$I-F_{eq.} > I-F_{axial}$

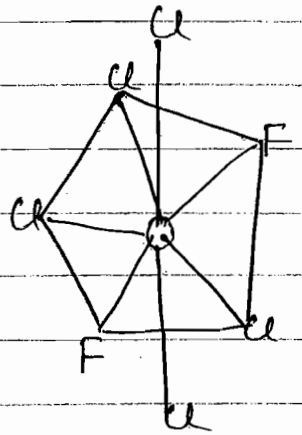
More bond angle ⇒ More S-character ⇒ More influence of Nucleus i.e. more electronegativity (χ).

More In PBP there are two types of angle (90°, 72°) Orb. on 90° having more S-character ⇒ more χ hence more electronegative atom does not want to form bond from axial side. Orb. on 72° having less S-char ⇒ less χ hence more χ atom will bind from this side.

Eg. IF_2Cl_5



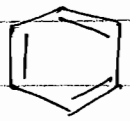
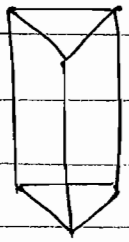
3 big Cl together



Only 2 big Cl together

A ⟨ ⟩ B A & B are isobal.

NET, GATE

Q ≡  &  str. are — Structural isomers.

* All molecules of world shows resonance.

More than 1 str.

Res. Str. of H_2

Eg. $H_2 \Rightarrow [H—H \longleftrightarrow H^+ H^- \longleftrightarrow H^- H^+]$

* Bonds are not fix. (It is electrostatic force) so it changes its length.

$H \overset{\leftarrow}{—} H \overset{\rightarrow}{} \longleftrightarrow H——H$

$H \overset{\rightarrow}{—} H \overset{\leftarrow}{} \longleftrightarrow H—H$

} More than one type str.

CONCEPT OF RESONANCE :

Given by Pauling

"There are many comp., which can't be represent by a single electronic str. they are represented by more the one electronic str. called Res. str. or canonical str. and this phenomenon of representation of a single spp by more than one electroninic str. is called "Resonance".

* All type Resonance are Hyperconjugation.

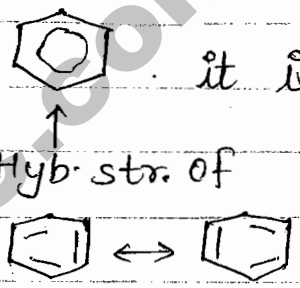
बेटा जी! Resonance जैसी कोई भी चीज इस दुनिया में नहीं है, It is only Hypothetical concept, Resonating str. are non real.

CRITERIA of Resonance :-

1) Resonance str. are non real.

2) ↔ the arrow, don't means interconversion.

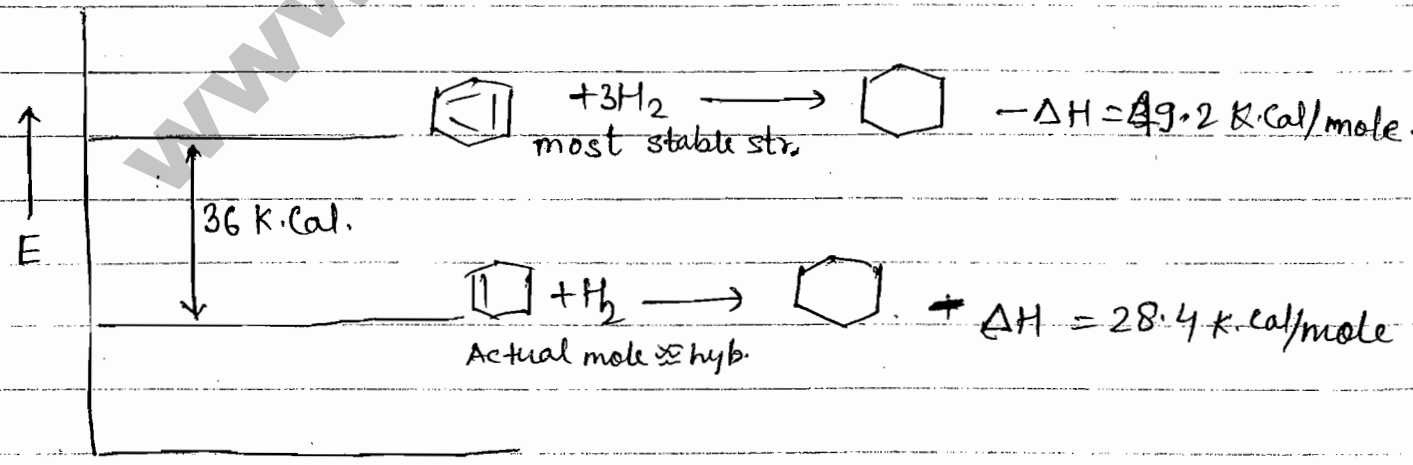
3) Res. Hybrid. is also non Real it is also a trick str.



4) Resonance energy

"It is the diff in the energies of theoretical Values & exp values".

"It is the diff. in the energies of most stable str. & actual str (some times consider resonance hybrid)"



* One = bond $+H_2 \rightarrow CH_3-CH_3$ $-\Delta H = 28.4$

3 = " $+3H_2 \rightarrow 3CH_3-CH_3$ $-\Delta H = 28.4 \times 3 = 85.2$

but in Benzene it is only 49.2 K.Cal/mole

Less bond angle b/w orb. i.e. less s-char. means less electro orb. i.e. Less influence of Nucleus

* ClF_3

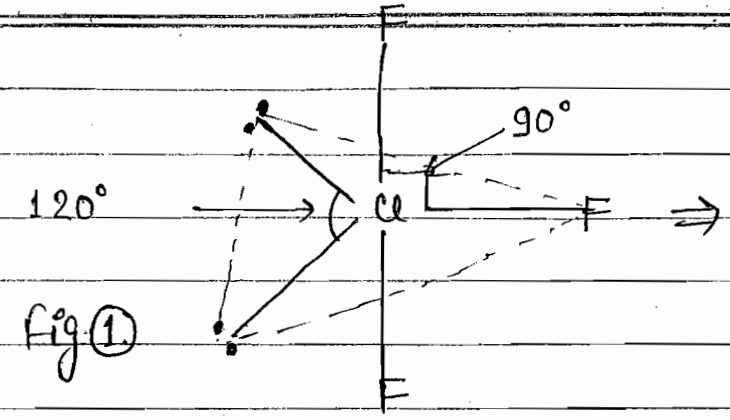


Fig ①

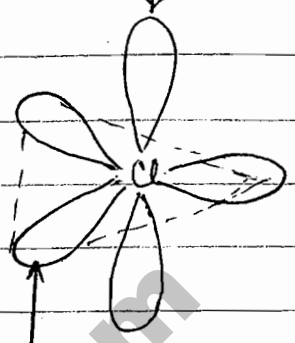


Fig ②

Q. Why l.p. on equatorial position?

A. From fig. ② it is clear that orb. forming more bond angle, are more electronegative.

Now if l.p. are in these (eq.) orb. then feel more nucleus attraction and will be stable.

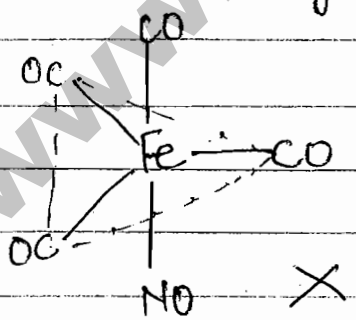
Orb. forming less bond angle, are less electro-ve

If l.p. are in these (axial) orb. then feel less nucleus attraction and will be unstable.

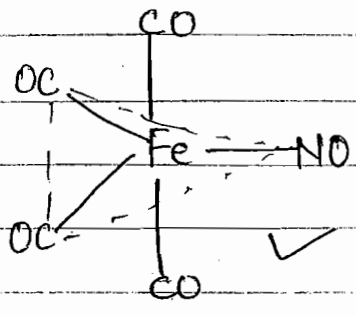
More bond angle b/w orbitals i.e. more s-character.

More s-cha. ⇒ more electronegative orb. i.e. More Near to Nucleus

* More π-accepting ligand prefers to equatorial position. in TBP.

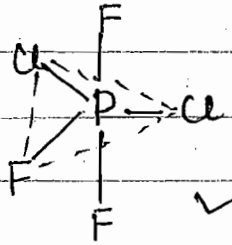


✗

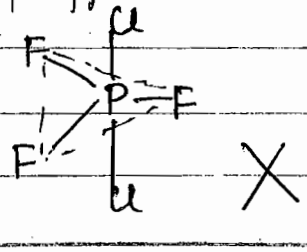


✓

* More electronegative atom prefferes to axial position in T.BP.



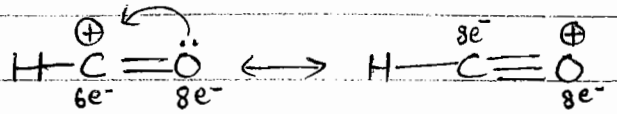
✓



✗

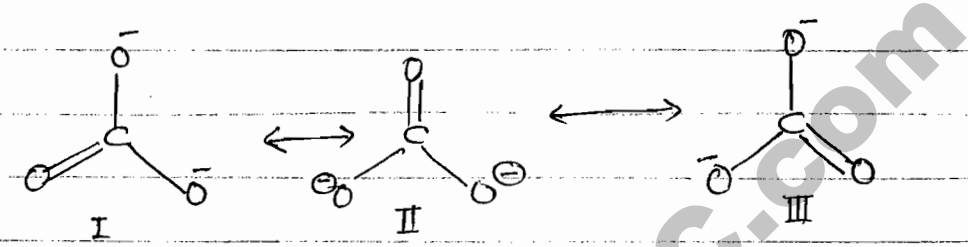
12|July|2014

Stability of Resonance structures:-



I II I < II

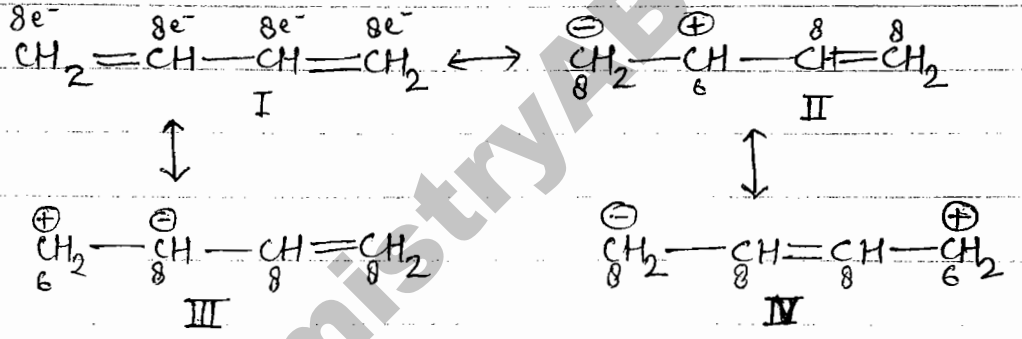
I = II = III



I II III

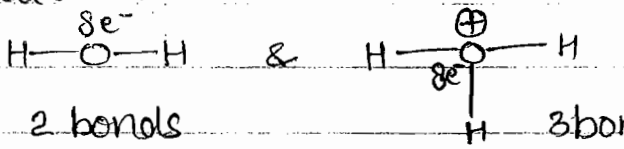
I > II > III > IV

opp. charge distance more



I II III IV

1) Those resonance str. are more stable which have complete octant and neutral.

2) More no. of bonds eg. 

2 bonds (less stable) & 3 bonds (More stable)

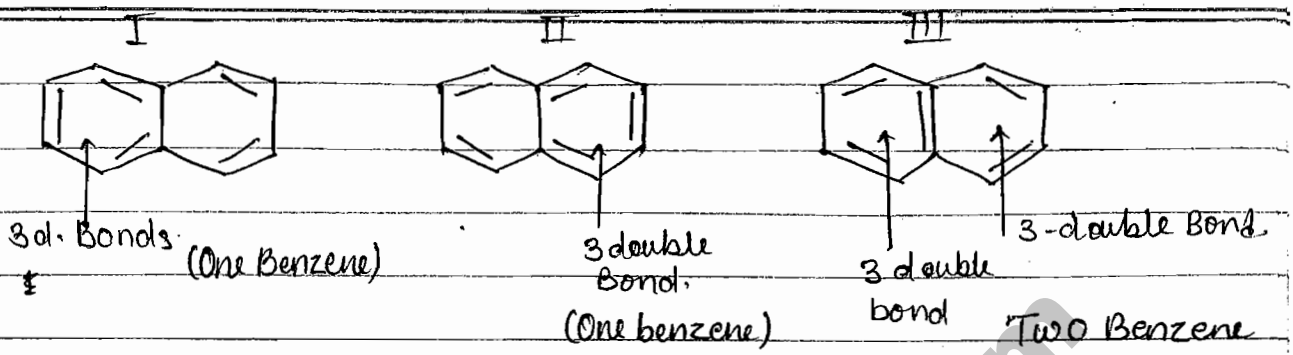
3) In charged str. same charges should be far apart & opp. charges should be closer.

4) Also observe stability of carbanion & carbocation.

5) Fries rule:- More the no. of benzene ring, more will be stability.

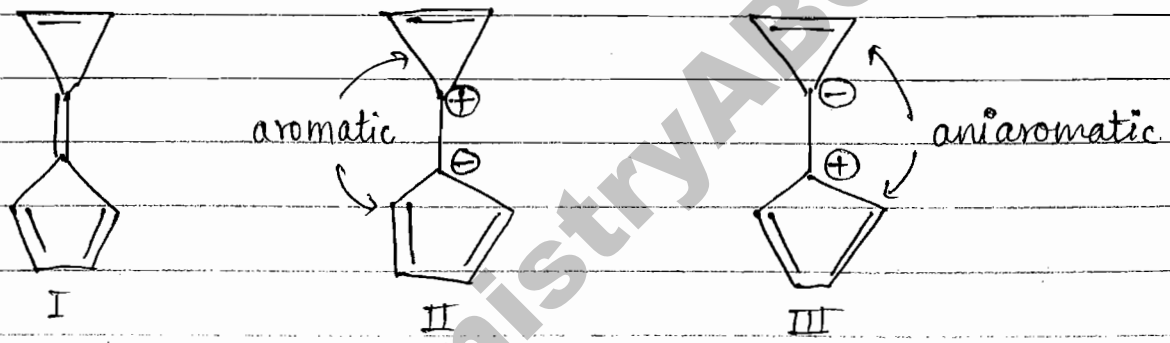
3 double bond.

Eg.



I = II < III

6) Some time also observe aromaticity.



III < I < II

Type of Resonance str.

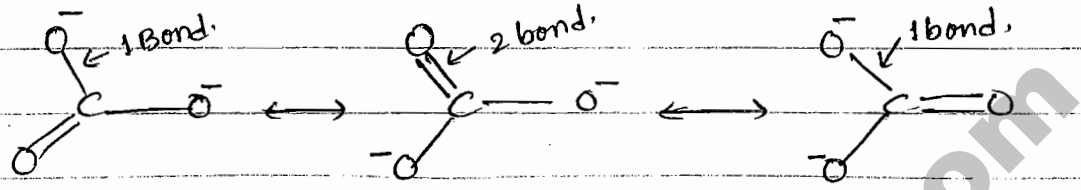
i) Isovalent resonance ⇒ No. of e^-, bonds same

ii) Heterovalent reso. str. ⇒ No. of e^-, bonds changes.

Application of Resonance:-

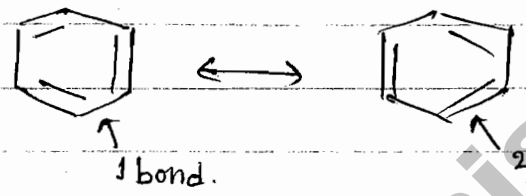
Due to resonance bond length, bond energy get change, & this can be studies with the help of bond order.

$$B.O. = \frac{\text{Total no. of bonds b/w two atoms in all stable reso. str.}}{\text{no. of stable Reso str.}}$$

Eg 

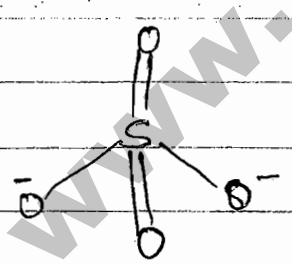
$$B.O. = \frac{1+2+1}{3} = \frac{4}{3} \Rightarrow 1.33$$

(3 ← no. of reso. str.)

Eg. 

$$B.O. = \frac{1+2}{2} = 1.5$$

Q. No. of stable R.S. & S—O bond order in SO_4^{--} is -



6 - Angle
⇓
6 Res. str.

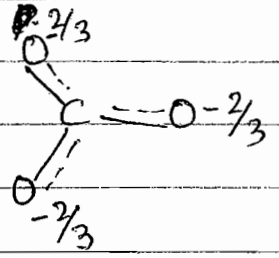
$$B.O. = 1 + \frac{\text{contribution of double bond on one atom}}{}$$

2 double bonds contributed among 4 oxygen. then, contribution of double bond on one oxygen $= \frac{2}{4} = \frac{1}{2}$

$$B.O. = 1 + \frac{1}{2} = 1.5$$

No of Angle = No. of res. str.

Q Find value of (-) charge on one oxygen atom.



two (-) charge distributed on 3 'O'.

Formal charge (F)

$$F = v - u + \frac{s}{2}$$

s — No. of shared e⁻ b/w bonds

u — No. of unshared e⁻

v — No. of valance e⁻

$$F = \text{Val. } \bar{e} - \text{l.p. } \bar{e} - \sigma \text{ bonds}$$

Eg. O = C = O

2 bonds = 4 e⁻

$$F = 6 - 4 + \frac{4}{2}$$

Two l.p

$F = 0$

Eg. O = C = O

$$F = 4 - 0 - \frac{8}{2}$$

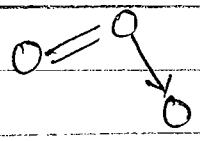
$= 0$

Eg. $\overset{\ominus}{C} \equiv \overset{\oplus}{O} \longrightarrow$ $F = 6 - 2 - \frac{6}{2} = (+1)$

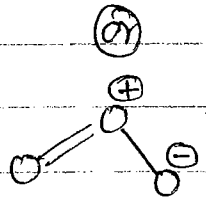
$$F = 4 - 2 - \frac{6}{2} = (-1)$$

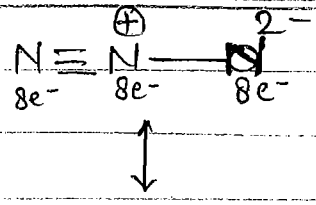
(-) charge = l.p.

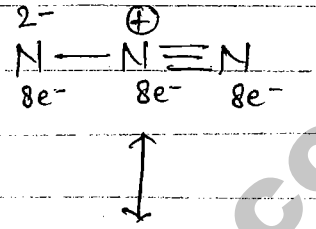
NET

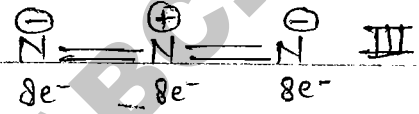
Eg.  Ozone

(or)



Eg.  I

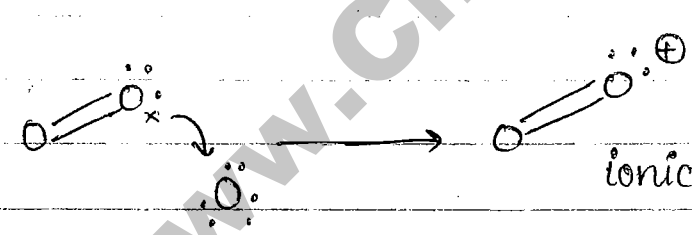
 II

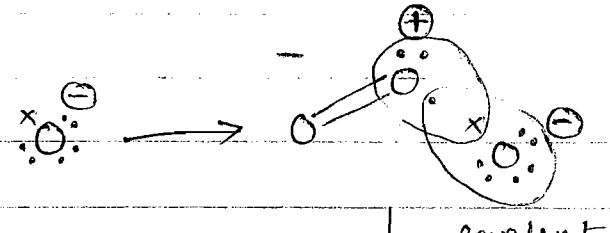
 III

$I \simeq II > III$

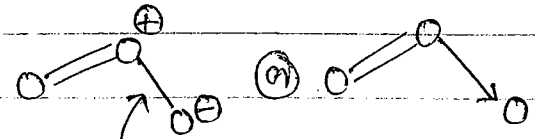
Stability.

Those s'ts are more stable which have more no. of zero charges with complete octate





covalent



Coionic bond.

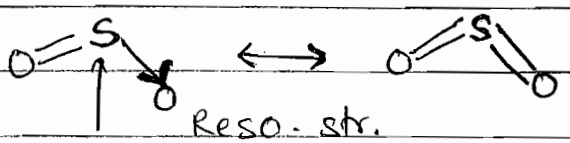
covalent + ionic

* H → C ⇉ N

O.N. +1 −1 −3
+3
⇓
+2

O ⇇ C ⇉ O

−2 +2 −2
+2
⇓
+4

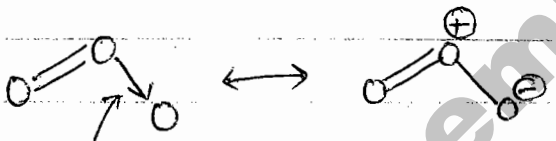
* 

donor atom.

Reso. str.

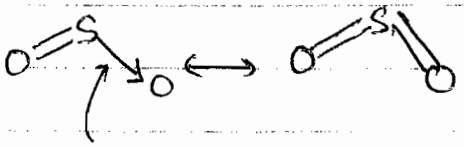
Donor atom

Donor atom of Second Period.

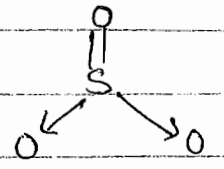


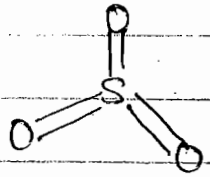
change this bond into σ bond with suitable charge on both atom

Donor atom of more than second period.



Change this bond into π bond.

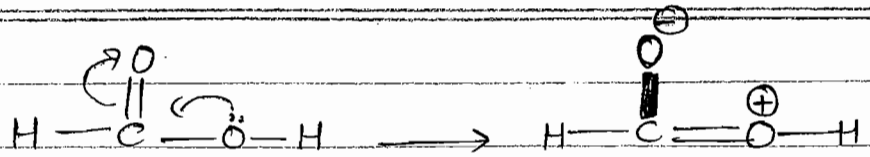
Q. find out σ & π bonds in. 

Ans.  3σ + 3π

* H—N⁺≡C⁻

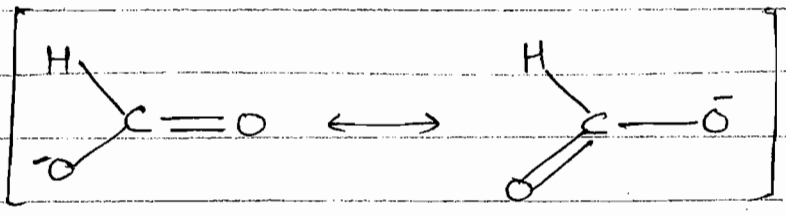
O.N. +1 −1 +3
−3
⇓
−3 +2

*



Heterovalent Resonating str.

*



Isovalent Resonance.

Q1 $\overset{+}{C}O$, CO, $C\overset{-}{O}_3^{-}$, CO_2 Bond Order arrangement ?

Q2 NO_2, $\overset{\oplus}{N}O_2$, $\overset{\ominus}{N}O_2$ " " " ?

Ans 1. $\overset{+}{C}O \Rightarrow 13e^- \Rightarrow 2.5$

$CO \Rightarrow 14e^- \Rightarrow 3.0$ (exception)

$CO_3^{2-} \Rightarrow 1.33$

$CO_2 \Rightarrow 2$ . . . . . .

C.N.R. Rav ⇒ Bharat Ratna.

HYDROGEN BONDING

—H—F·····H—F·····H—F··H—F···

* Formed by more electronegative atoms (F, O, N).
* H.B. is Weak bonding

2-30 KJ/mole

H.B Energy 1/10 of covalent bond.

Q. In H_2O, O—H bond energy ⇒ 129 K.J/mole, find H.B. energy.

H.B. energy = $\frac{1}{10}$ of Covalent bond.

$= \frac{129}{10} = 12.9$ K.J/mole

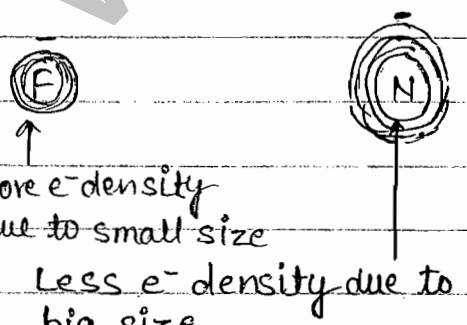
Q. H.B. stability.

N—H···:F I (More e⁻ tight bonded with Nucleus)

N—H···O II

N—H···N III (loosely e⁻ bonded with Nucleus.)

III > II > I



More e⁻ density due to small size

Less e⁻ density due to big size.

O—H···F⊖ I

O—H···O⊖ II

O—H···N⊖ III

I > II > III

$F^{\delta-}—H^{\delta+}\cdots F$ I

$O^{\delta--}—H^{\delta++}\cdots O$ II

$N^{\delta-}—H^{\delta-}\cdots N$ III

I > II > III

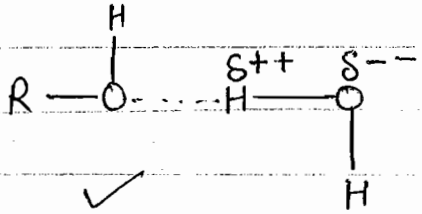
$\delta^+ < \delta^{++} < \delta^{+++}$ | $\delta^+ > \delta\delta^+ > \delta\delta\delta^+$

I $F^{\delta-}—H^{\delta+++}\cdots F^{\ominus}$

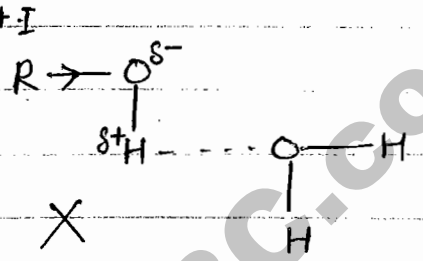
II $O^{\delta--}—H^{\delta++}\cdots O^{\ominus}$

III $N^{\delta-}—H^{\delta+}\cdots N^{\ominus}$

I > II > III

* 

✓



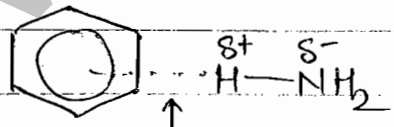
✗

Hydrogen Bonding

- σ H.B.
  - Intra
  - Inter
- π-H.B.
  - Intra
  - Inter

* 

H.B. with π bonds

*  (Ammonia in Benzene)

H.B. with π e⁻ (bonds)

HF shows H.B. in liq. phase as well as in gasious phase.
H_2O shows H.B. in liq. only.

No. of Hydrogen Bonds.

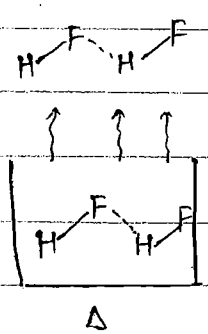
	H.B.
H_2O	3.59 ≈ 4
HF	2 ← 2 atoms are responsible for H.B. (H&F)
NH_3	4 ← 1 N + 3 H Responsible for H.B.
$R-O-R$	0 ← No any atom forms H.B.
H_2S	0

No. of H.B. = No. of Atoms ~~in~~ Responsible for H.B. except H_2O.

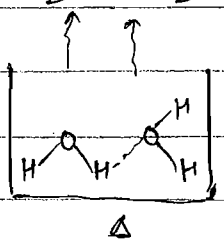
Q. B.P. order among CH_4, NH_3, H_2O, HF ?

$H_2O > HF > NH_3 > CH_4$

H_2O : Strong H.B.
HF : Strongest H.B. But B.P. $< H_2O$ why ?
NH_3 : Weak H.B.
CH_4 : No. H.B.



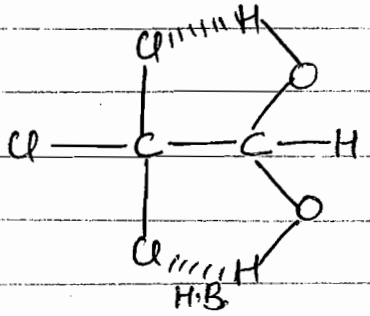
← Not all H.B. Breaks i.e. less energy required i.e. Less B.P.

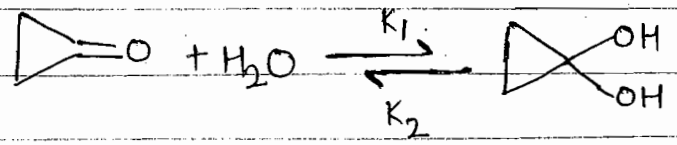


← No H.B. in Vapour phase i.e. all H.B. Breaks. means more energy required to break bond Hence more B.P.

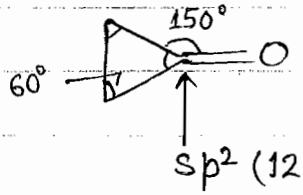
* $CCl_3CHO + H_2O \longrightarrow CCl_3CHO \cdot H_2O$

Chloral — chloral hydrate



Q 

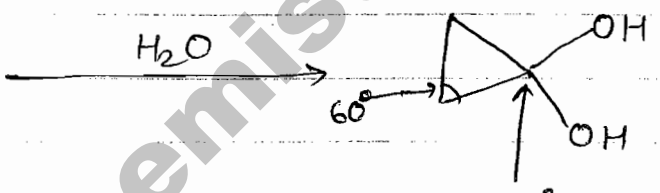
✓a) $K_1 > K_2$ b) $K_1 < K_2$



Sp^2 (120)

More Angle strain

(Less stable)

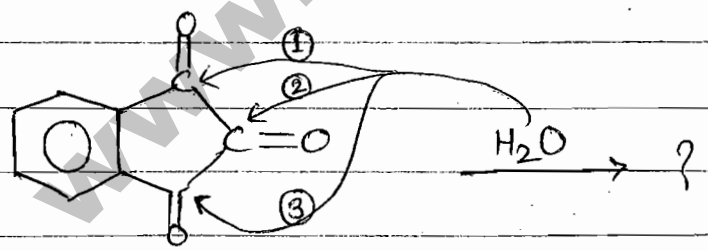


Sp^3 (109°)

Less angle strain

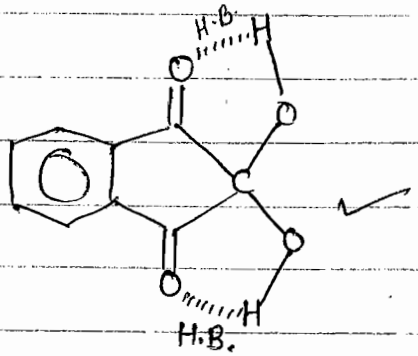
(More stable)

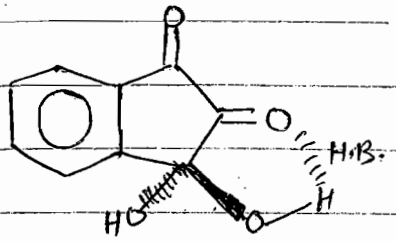
*



Ninhydrin

"Tri keto hydrendin"





X

H. B.

Symmetric H.B. — Asymmetric H.B.

Q Arrange order

$KF + HF \rightleftharpoons KHF_2$ (K_1)

$KCl + HCl \rightleftharpoons KHCl_2$ (K_2)

$KBr + HBr \rightleftharpoons KHBr_2$ (K_3)

$K_1 > K_2 > K_3$

$KHF_2 \longrightarrow K^+ \; HF_2^-$

$[F^- \cdots H — F]$ ⟸ H.B. is very strong i.e. why

Both 'F' identical (1 signal in ^{19}F-NMR)

$KHCl_2 \longrightarrow K^+ \; HCl_2^-$

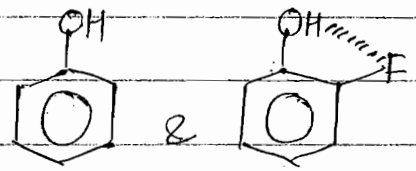
H.B. in this case is symmetric H.B. (Both F···H & H—F bonds same strong).

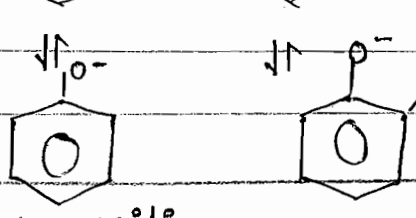
$[Cl^- \cdots H — Cl]$

Weak Strong

Both Bonds (Cl···H & H—Cl) are diff. ⇒ Asymmetric H.B.

Q Acidic strength ?



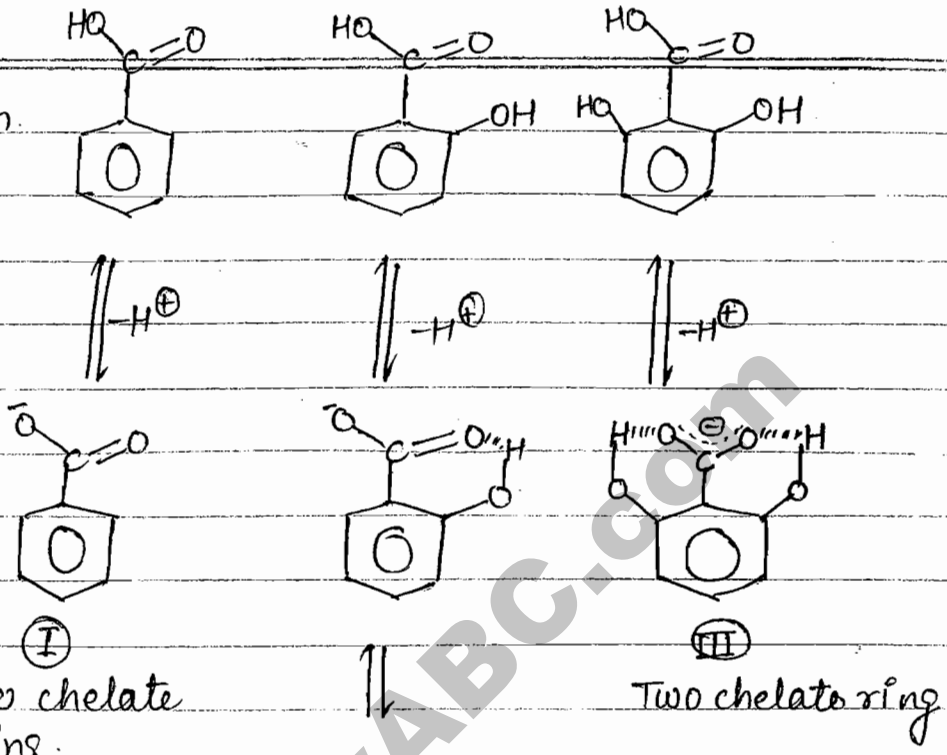


H ← H^+ not free

less acidic

More acidic

Q Acidic strength

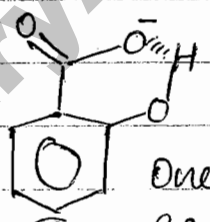


(I) No chelate ring.

(III) Two chelate ring

Conjugate base stability.

III > II > I



(II) One chelate Ring

More stable conj base, more will be acidic.

STRUCTURE OF ICE

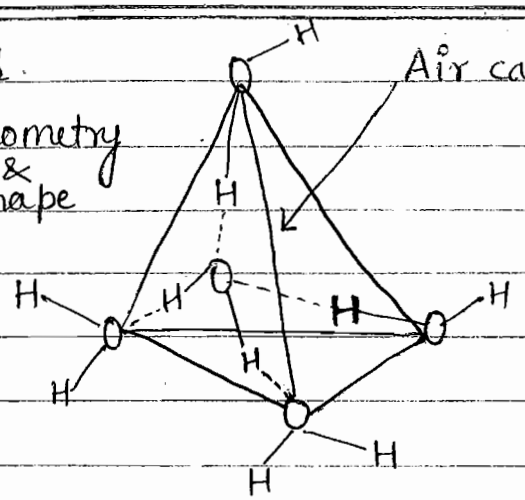
Str. and properties of ice, based upon hydrogen bonding. at diff temp & press. ice adopt diff. kinds of str. having diff. properties. the most common form of ice is ice-I

Ice shape - Td.
Water → Bent

14/07/2014

(46)

Td Geometry & shape



At 4°C all these 5 H_2O molecules are closer hence max. density of H_2O is at 4°C

Due to air cavities, ice become light weighted i.e. why it float on water.

Unit of Ice ($5 H_2O$)

Snow ⇒ White ⇒ Imperfect crystal ⇒ Less density.
Ice ⇒ Transparent ⇒ Perfect crystal ⇒ More density

Ice is a non conductor ⇒ No ionic movement.

Ice-III (500 atm & 200°C) ⇒ Hot ice (or) Fire Ice.

* Bi, Ge & Ga also expands on freezing like ice. i.e. why density decreases.

Q. What is the shape of $ICl_6^{\ominus}$? Perfect Octahedral. because lone pair is stereo chemically inactive.

lone pair

Stereochemically active l.p.
(l.p shows distortion)

Stereochemically Inactive l.p.
(l.p shows no distortion)

Etc Vander wall radius > Covalent Radius.

Stereochemically Inactive lp.

Central Atom size - large (5, 6, 7th period)

Large size of sorrounding atom. (Cl, Br, I)

Q. $\bar{I}F_6$ & $\bar{I}Cl_6$ which one is base?

$\ddot{I}F_6$ (Active lone pair) $\Rightarrow$ Base.

$\ddot{I}Cl_6$ (Inactive lone pair) $\Rightarrow$ No Base. even lone pair +nt.

* In XeF_6 lp. of Xe is ~~no~~ neigther perfectly active nor perfectlly inactive i.e. XeF_6 found in 3 forms.

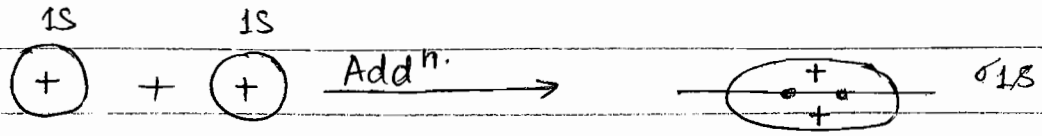
* XeF_6 is more stable in Distorted octahedral.

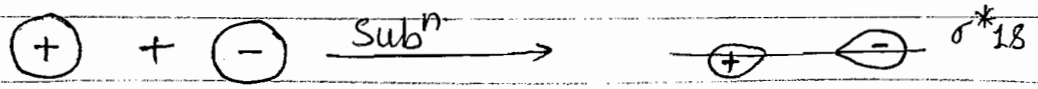
MOLECULAR ORBITAL THEORY [MOT]

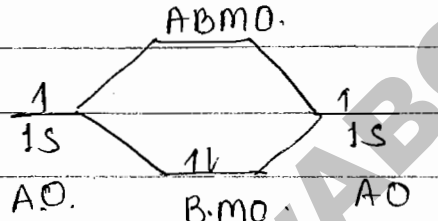
1) Atoms combine to give molecule. A.O. combine to form M.O.
2) M.O. are non real
3) M.O. are formed by A.O. via hypothetical mixing, two methods are known for hypothetical mixing.
   i) LCAO (Linear combination of Atomic orbitals).
   ii) United ATOM method (UA method)

   M.O. ⇒ Polycentric ⇒ Non Real.
   A.O. ⇒ Monocentric ⇒ Real
   H.O. ⇒ Monocentric ⇒ Non real. (H.O. = Hyb. Orb).
4) The no. of M.O. is equal to the No. of A.O.
5) Mixing of orb. May be two type.
   i) Additive Mix.
   ii) Subtrative Mix.
6) By additive mix. BMO forms, it means which have more probability of finding e^- therefore they are in low in energy.
7) By subtrative mix. ABMO forms. ⇒ Less probability of finding e^- ⇒ High in energy.
8) M.O. also follow those rules which are followed by A.O.
   i) Auf-bau rule.
   ii) Hund's "
   iii) Pauli "
9) Conditions of M.O. formation:
   Symmetry similar, Less energy diff.

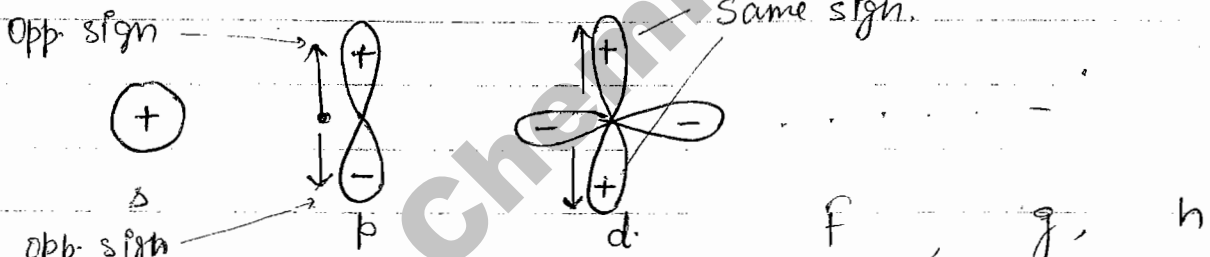
LCAO





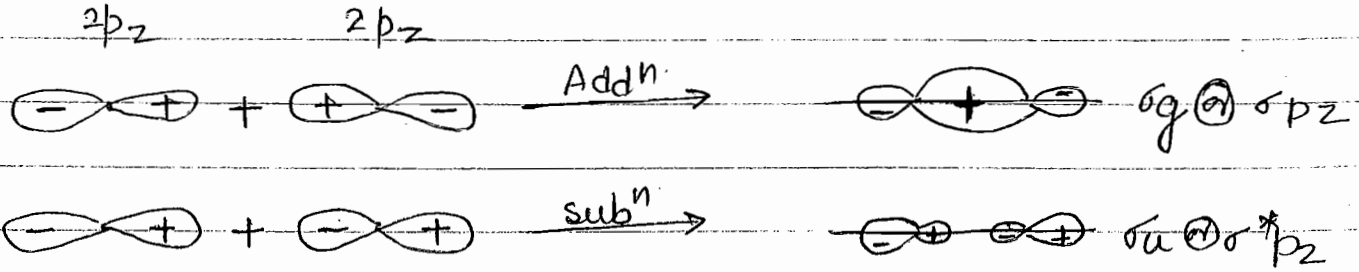


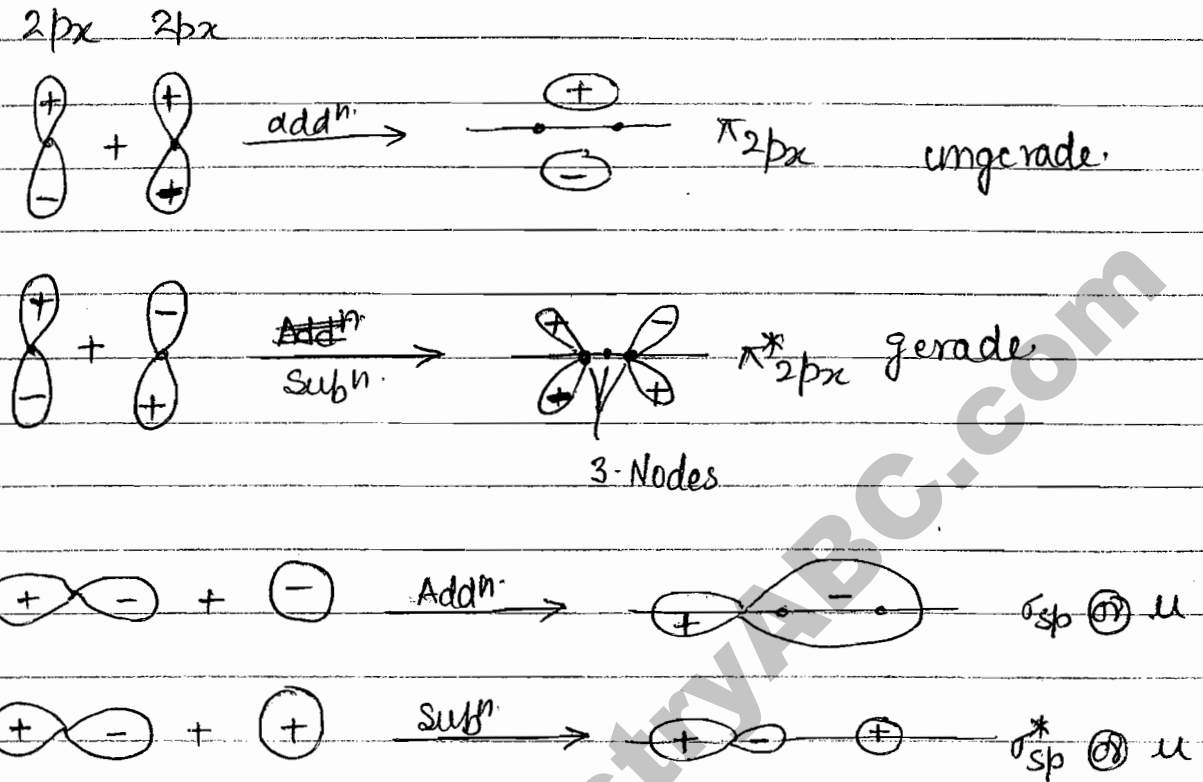
imp Symmetry of Orb.



s, d, g ⇒ centrosymmetric ⇒ gerade.

p, f, h ⇒ Non " " ⇒ Ungerade





Energies of M.O.

A.O.	A.O.	BMO	ABMO
1s	1s	σ1s	σ*1s
2s	2s	σ2s	σ*2s
2pz	2pz	σ2pz	σ*2pz
2px	2px	π2px	π*2px
2py	2py	π2py	π*2py

$Li_2, Be_2, B_2, C_2, N_2$

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \underbrace{\pi_{2px} \; \pi_{2py}}_{\text{same}} < \sigma 2p_z < \underbrace{\pi^*_{2px} \; \pi^*_{2py}}_{\text{same}} < \sigma^* 2p_z$$

* Less than 14 or 14 e^- ⇒ σ comes later.
* More than 14 e^- ⇒ σ comes Before.

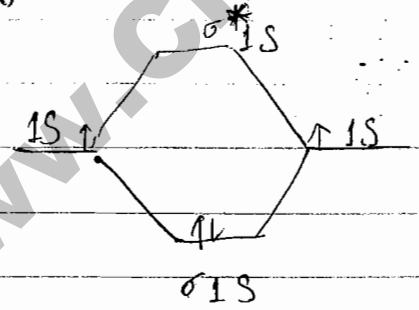
O_2, F_2

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \begin{matrix}\pi 2p_x \\ \pi 2p_y\end{matrix} < \begin{matrix}\pi^* 2p_x \\ \pi^* 2p_y\end{matrix} < \sigma^* 2p_z$$

Non-Co Crossing Over Rule/Sym. Rule:-

If the two energy states having same Sym. are closer to eachother then the lower level is decreased further in energy & the higher level is increased further in energy. This depend upon energy diff. b/w A.O. If the energy diff. is less then 7 e⁻V/M. mixing takes place

M.O. Diagram. / B.C. / Bond Strength / Bond Energy.



$$B.O. = \frac{BMO - ABMO}{2}$$

$$B.O. = 1$$

Arrange Bond Energy among H_2 $H_2^{\oplus}$ H_2^{-}

B.O. 1 ½ ½

$$H_2 > H_2^{\oplus} > H_2^{\ominus}$$

Fe^{2+} more stable in soln. phase.

Fe^{3+} " " " solid "

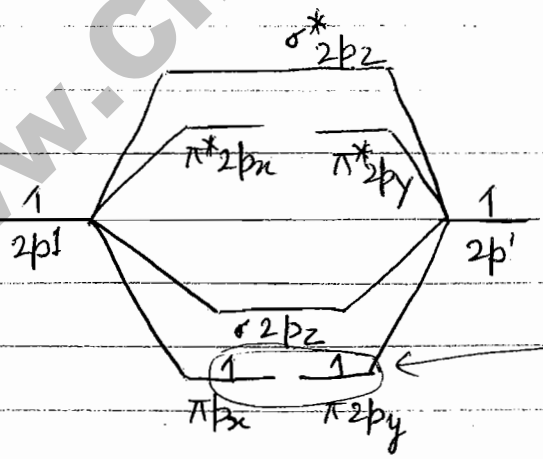
	H_2^+	H_2^-
σ^*_{1s}	—	↑ ← e^- in ABMO. (Unstable)
σ_{1s}	↑ ← e^- in BMO. (Stable)	↑↓

Bond length. $H_2^+ < H_2 < H_2^-$

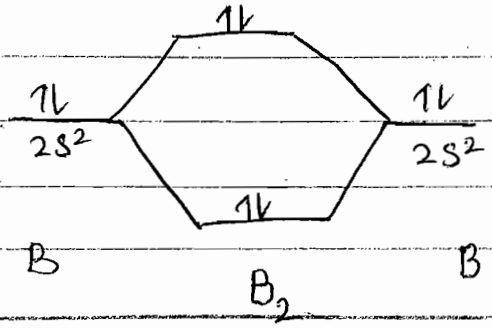
$1e^-$ $2e^-$ $3e^-$

In H_2^+ one ~~one~~ e^- attracted by 2 Nucleus hence less bond length. even bond order is 0.5 In H_2^- $3e^-$ are attracted by 2 Nucleus hence more bond length.

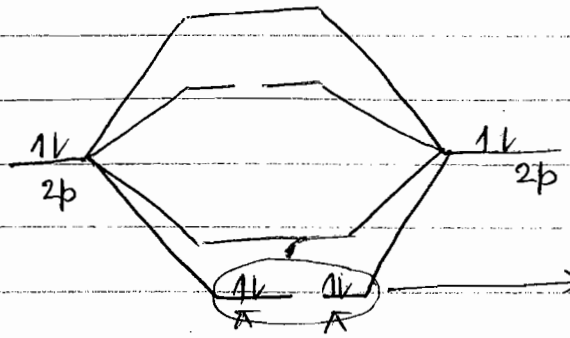
* If B.O. is zero then no existance of molecule Eg. ~~He_2~~, Ne_2



Two unpaired e^- hence no. unpaired. bonding b/w Boron atoms. even B.O. = 1

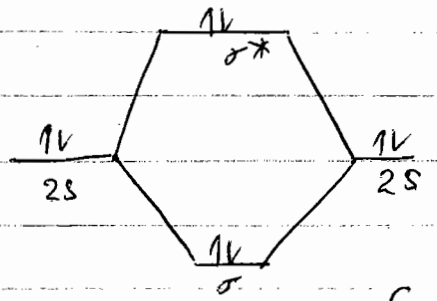


B 1 1B



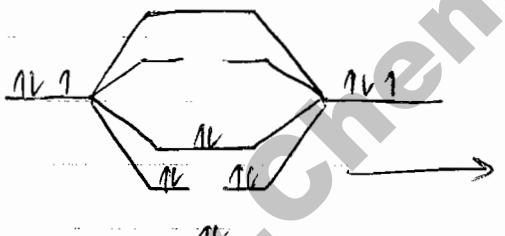
→ $4e^-$ in π obitals i.e. why. In $C \overset{\pi}{\underset{\pi}{=}} C$ there are two π bond.

B.O. = 2



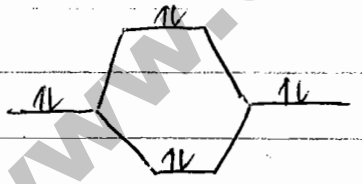
C C C

C_2



$\overset{\ominus}{C} \overset{\pi}{\underset{\pi}{\equiv}} \overset{\ominus}{C}$ Acyt Acetylide ion,

B.O. = 3.



C^- C_2^{2-} C^-

Coefficient

1	s
2	p
3	d
4	f

Oxy = Life, gen = forming

$N_2 > O_2 > Ne > CO_2$
78% 21% & Ar 1.9% 1.3%

Imp

Q Arrange bond strength. of s-s, sp, p-p, p-d, d-d. bonds.

s—s < s—p < p—p < p—d < d—d.

1 × 1 1 × 2 2 × 2 2 × 3 3 × 3

1 2 4 6 9.

Imp Molecular electronic configuration.

$C_2 = KK\ \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2$

(or)

$C_2 = KK\ \sigma_g^2, \sigma_u^{*2}\ \pi_u^4$

↑ for Ist Shell.

O_2^+ ⇒ oxygenyl ion, O_2^- = Super oxide, O_2^{2-} = Peroxide

$O_2 = KK.\ \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$

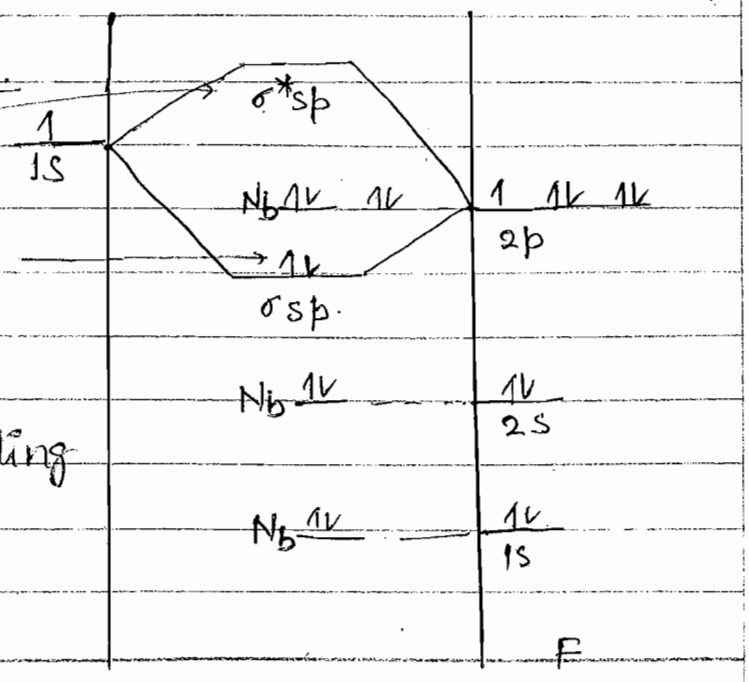
M.O. Diag. of Hetero Atoms.

ABMO

HOMO ⇐ B.M.O

M.O.D of 'HF'

Nb = Non Bonding



GATE 2010, 2011

Which is HOMO in HF — ~~Non bonding~~ σ bonding.

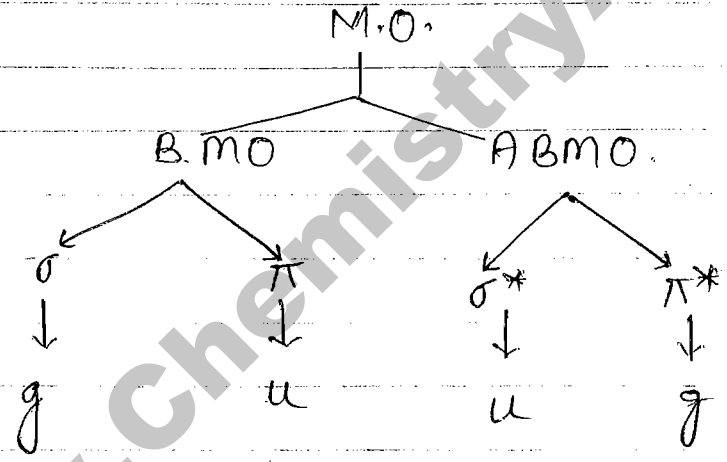
* Since electronegativity of F is very much than H. i.e. why 1s, 2s, 2p all are lower in energy tha that of 1S of H atom.

GATE

Q Which is the Highest Occupied orbital in H.F. ?

Ans In this ques not asking about M.O. hence highest occupied orb. is Non bonding.

Most gap →



Mol. Orb. Diag. of CO (Old View)

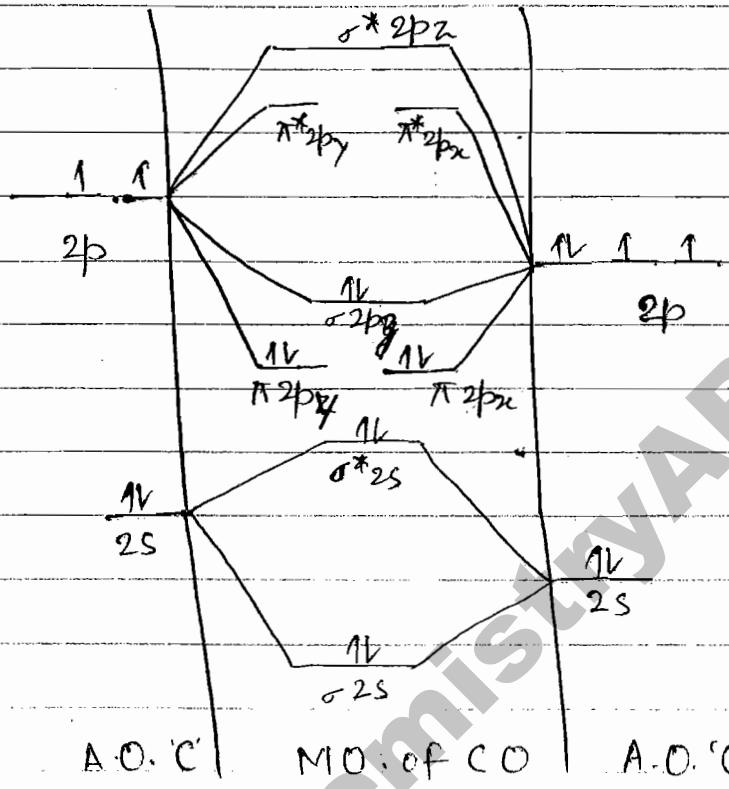
Isostere

Same no. of e^-

Same str.

total atoms.

Eg. O=C=O & N≡N→O



The donar ability and bond length are not explained by above diag. hence diagram rejected.

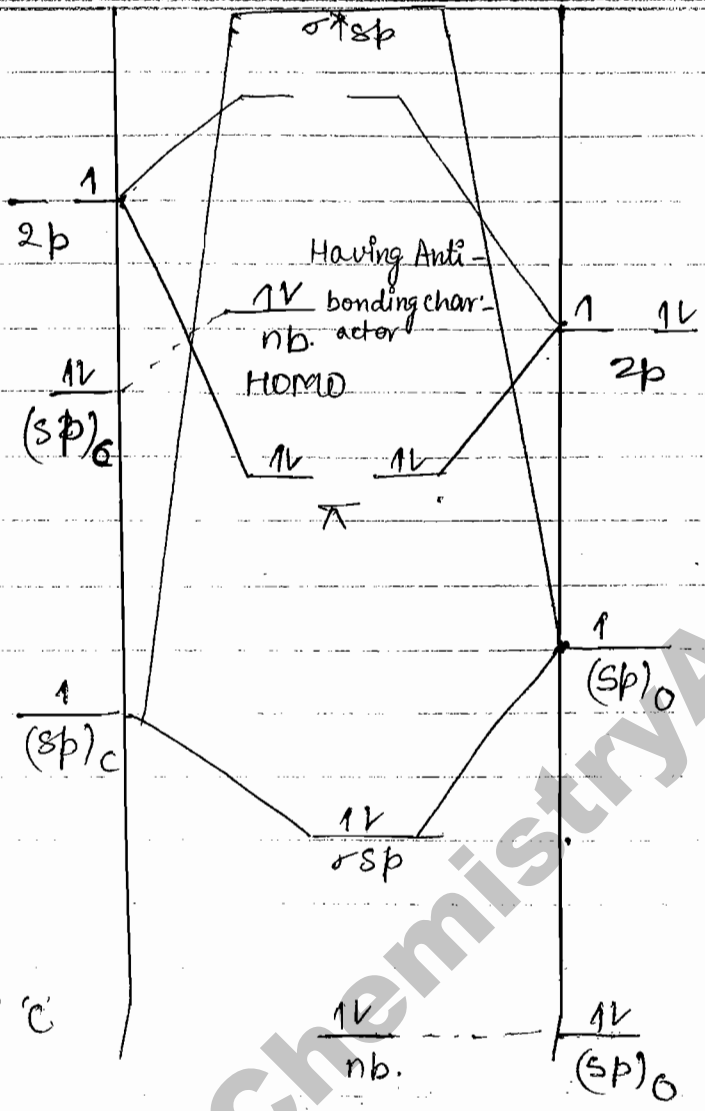
Coulson Modification :-

C = K ⇅ 2s | ↑ ↑ 2p

= K ⇅ ↑ (sp hyb) | ↑ (2p Un hyb.)

O = K ⇅ ↑ | ↑ ⇅

= K ⇅ ↑ (sp hyb.) | ↑ ⇅ (2p Unhyb)



$$B.O. = \frac{6-0}{2}$$

$$B.O. = 3$$

Modern Molecular Orbital Diagram of CO :-

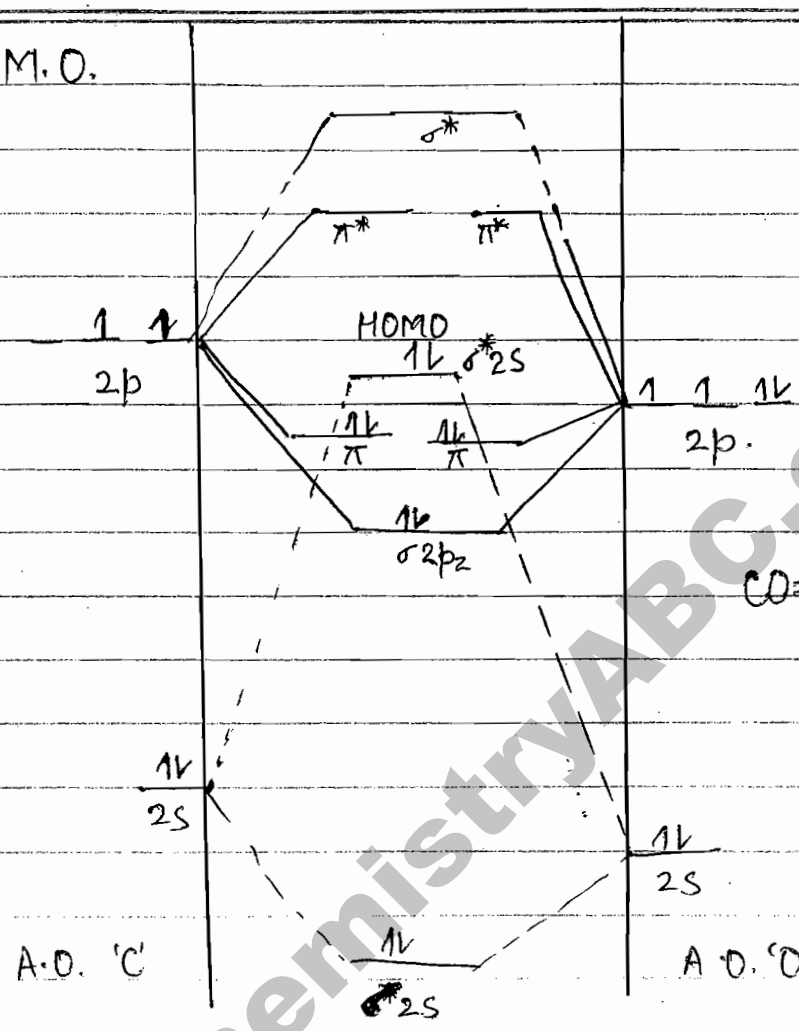
$$B.O. \text{ of } CO = \frac{8-2}{2} = 3$$

$$B.O. \text{ of } CO^{+} = \frac{8-1}{2} = 3.5$$

CO is good $\underline{\sigma}$ donor (because it donate e^- from σ^*2s)

CO is $\underline{\pi}$ acceptor (because it accepts e^- in $\underline{\pi^*}$ ABM.O.)

MODERN M.O. of CO :-



HOMO of 'CO' is σ^*_{2S}

CO ⇒ Diamagnetic

CO^+ ⇒ Paramagnetic

M.O. Diagram of NO.

NO ⇒ Paramagnetic

⇒ One unpaired e⁻

⇒ Highly reactive.

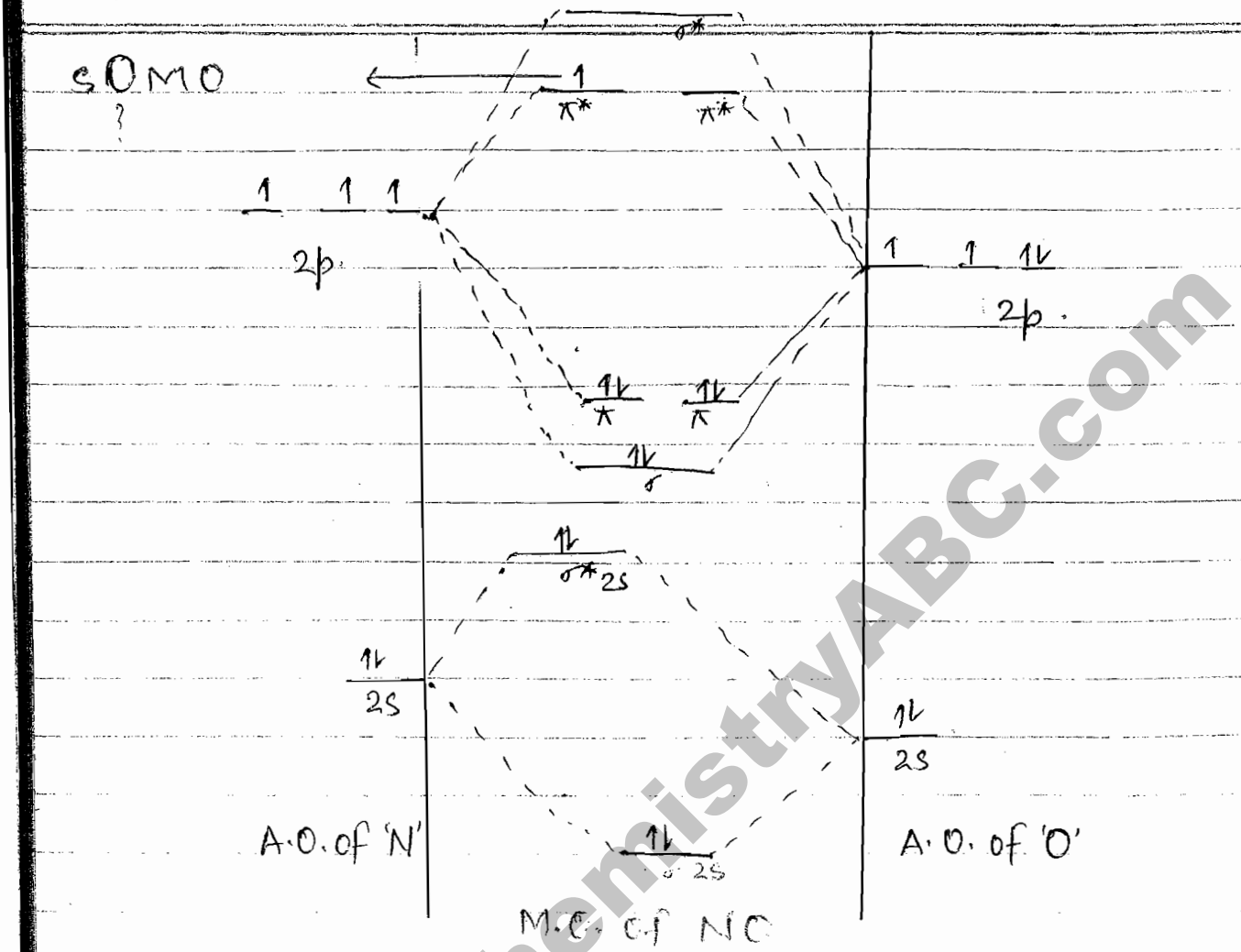
B.O. NO = $\frac{8-3}{2} = 2.5$

B.O. NO^+ = $\frac{8-2}{2}$

= 3

One e^- donor lig. ⇒ Hemidentate

Three e^- " " ⇒ sesquidentate



Q $Fe(CO)_5 \xrightarrow{NO}$?

One CO ⇒ 2 e^- ⇒ 3CO ⇒ 6 e^-

One NO ⇒ 3 e^- ⇒ 2NO ⇒ 6 e^-

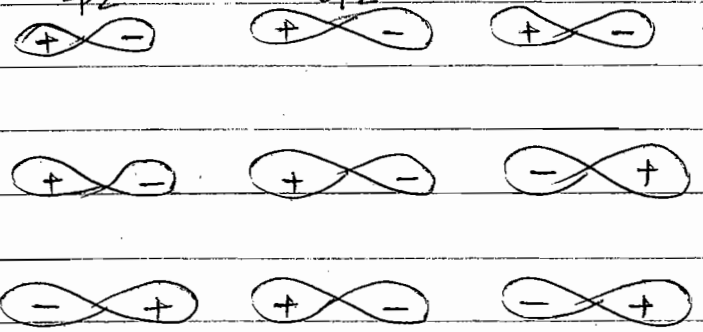
$Fe(CO)_5 \xrightarrow{2NO} [Fe(CO)_2(NO)_2]^{2+}$

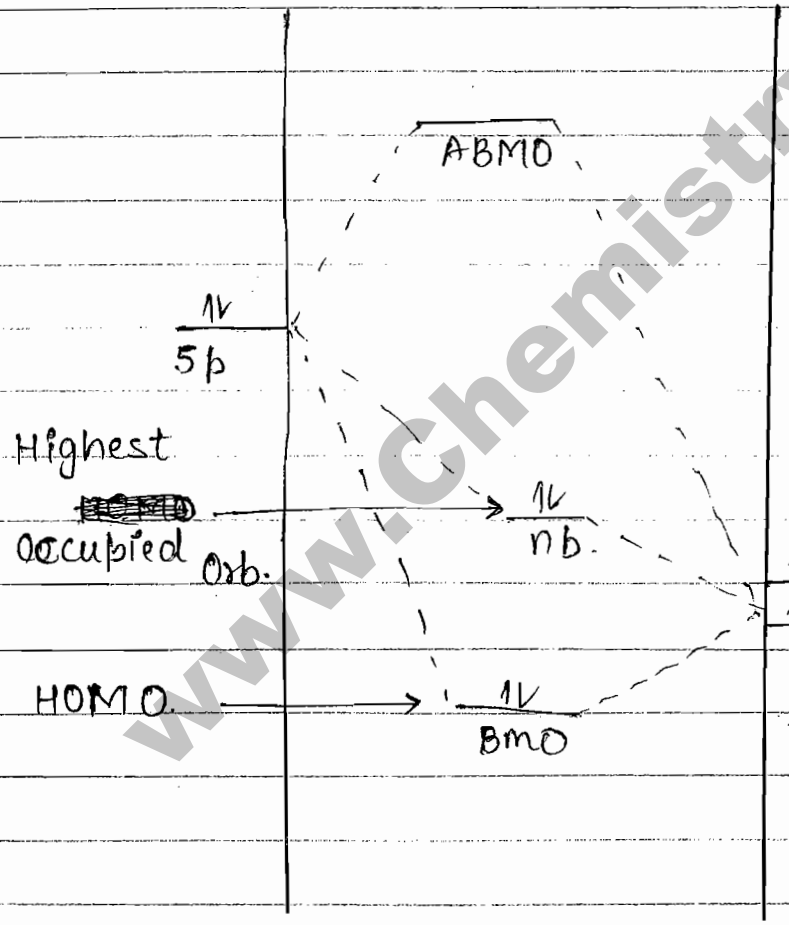
SOMO ⇒ Singly Occupied Molecular Orbital.

M.O.D. of Polyatomic Spp.

He = $1s^2$
Ne = $2s^2 2p^6$
Ar = $3s^2 3p^6$
Kr = $4s^2 4p^6$
Xe = $5s^2 5p^6$
Rn = $6s^2 6p^6$

F — $2p_z$ | Xe — $5p_z$ | F — $2p_z$





B.O. of XeF_2

$= \frac{2-0}{2} = 1$

F — Xe — F

↑

½ B.O. for Xe—F

B.O. one for XeF_2 Mol.

03/AUG/2014

DIPOLE MOMENT ($\vec{\mu}$) :-

It is a vector quantity.

It is characteristic of polar bond, and defined as prod. of magnitude of charge and distance b/w charges.

$\overset{\delta+}{H} \longrightarrow \overset{\delta-}{Cl}$ $\qquad \vec{\mu} = |q| \cdot l$

$+q \leftarrow l \longrightarrow -q$

Unit

S.I unit: Colomb × met.

Non S.I unit.

$l = 1\,A^\circ = 10^{-10}\,m = 10^{-8}\,cm$

$q = 1.6 \times 10^{-19}$ col. $= 4.8 \times 10^{-10}$ esu

$$\vec{\mu} = q \cdot l = \underset{esu}{4.8 \times 10^{-10}} \times \underset{cm}{10^{-8}}$$

$$\vec{\mu} = 4.8 \times 10^{-18}\ esu \cdot cm$$

$\boxed{10^{-18}\ esu \cdot cm = 1\,D\ (Debye)}$

1) % Ionic character in Co-valent Bond:

a) Dipole moment Method.

$$\%\ I.C. = \frac{\mu_{obs}\ \text{(Experimental)}}{\mu_{cal.}\ \text{(Theoretical)}} \times 100$$

Q Dipole moment of a molecule ~~1.37 A°~~, 1.03 D

$l = 1.37\,A^\circ$, % ionic character ?

$\mu_{obs} = 1.03\,D$

$\mu_{cal} = q \cdot l \Rightarrow 4.8 \times 10^{-10}$ esu $\times 1.37 \times 10^{-8}$ cm

$\vec{\mu}_{cal.} = 4.8 \times 1.37 \times 10^{-18}$ esu.cm.

$= 4.8 \times 1.37 D = 6.576$

% ionic $= \frac{\mu_{obs}}{\mu_{cal.}} \times 100 \Rightarrow \frac{1.03}{6.576} \times 100 \Rightarrow 15.66\%$

b) Electronegativity Method

By Hanny - Smith eqn.

$$\% \text{ I.C.} = 16 (\chi_A \sim \chi_B) + 3.5 (\chi_A \sim \chi_B)^2$$

Q Find % I.C. in NF_3

F = 4 N = 3

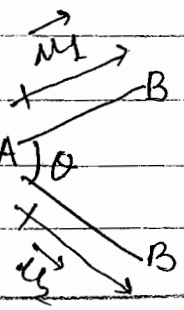
$\chi_N \sim \chi_F = 1$

% I.C. $= 16 \times 1 + 3.5 \times (1)^2$

$= 19.5$

2) Nature of Molecules :-

covalent mol. may be polar or non polar if $\vec{\mu} = 0$ then mol. suppose to be non polar if its value is greater than 0 zero, then mol. will be polar. Net dipole moment μ is observed by vector summation.



$$\text{Net } \vec{\mu} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos\theta}$$

$$\vec{\mu}_{net} \propto \sqrt{\cos\theta}$$

$$\vec{\mu}_{net} \propto \frac{1}{\sqrt{\theta}}$$

Factor $\vec{\mu}$

i) $\propto (\chi_A \sim \chi_B)$

ii) $\propto q$

iii) $\propto l$ (Bond length)

iv) $\propto \frac{1}{\sqrt{\theta}}$

i) Diatomic spp. $Cl_2, N_2, O_2, F_2, Br_2$ Non polar. $\vec{\mu} = 0$

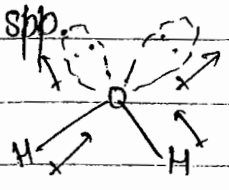
HCl, HBr, ClF, BrF Polar. $\vec{\mu} \neq 0$

ii) Triatomic spp. $BeCl_2$, CO_2, BeF_2 Non polar $\vec{\mu} = 0$

COS $\Rightarrow$ $\overset{\longrightarrow}{O}=C=\overset{\longrightarrow}{S}$ $\vec{\mu} \neq 0$

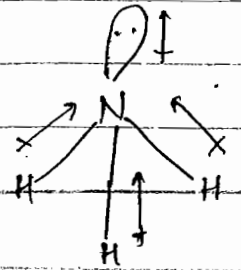
iii) Poly atomic spp.

H_2O



$\mu \neq 0$ l.p. dipole moment always away from c. atom.

NH_3



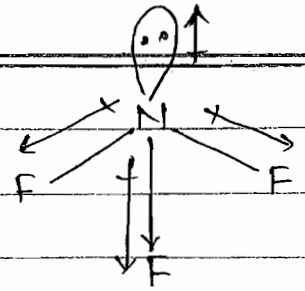
$\mu \neq 0$

$\vec{\mu}$ of ionic comp. always +ve value (not zero).

Dipole moment (μ) always +ve quantity.

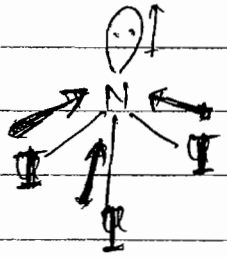
(CA)

NF_3



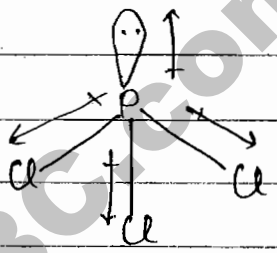
$\vec{\mu}_{net}$ Subtractive

NH_3



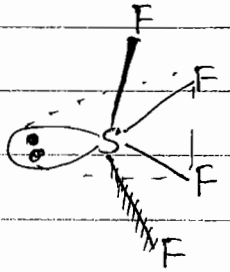
$\vec{\mu} \neq 0$

PCl_3



$\vec{\mu} \neq 0$

SF_4

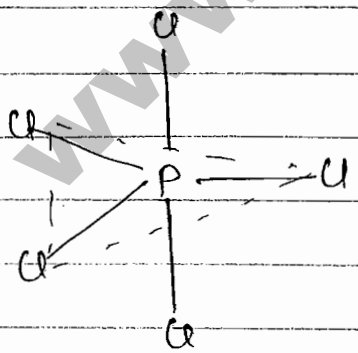


$\mu \neq 0$

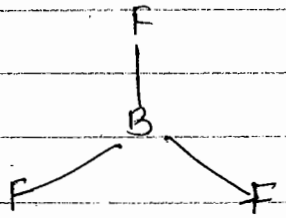
* $\vec{\mu}$ NaCl > $\vec{\mu}$ HCl

ionic > covalent

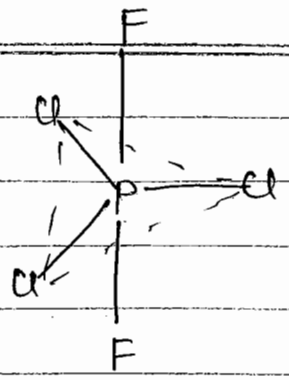
* PCl_5 $\Rightarrow$ $K^+ MnO_4^-$ ionic comp. with covalent bond



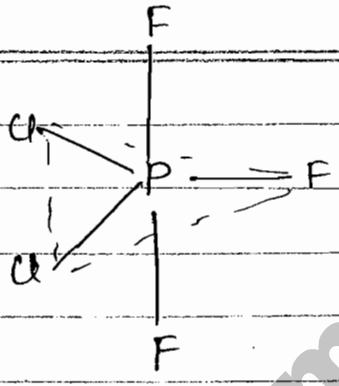
$\vec{\mu} = 0$



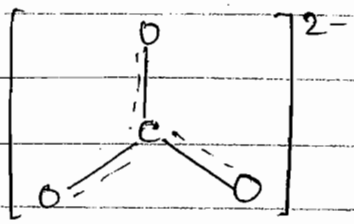
$\vec{\mu} = 0$



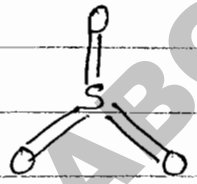
$\vec{\mu} = 0$



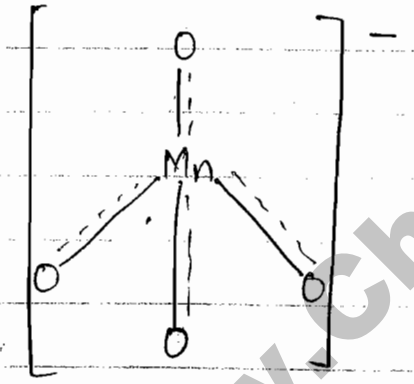
$\vec{\mu} \neq 0$



$\vec{\mu} = 0$

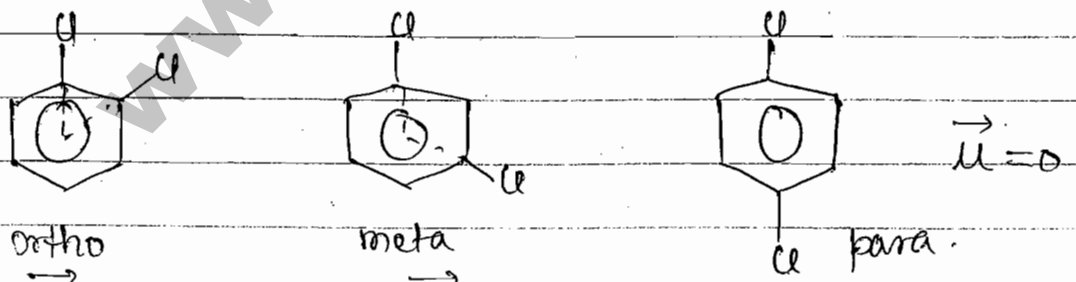


$\vec{\mu} = 0$



$\vec{\mu} = 0$

* SO_4^{-} $\vec{\mu} = 0$



$\vec{\mu} = 0$

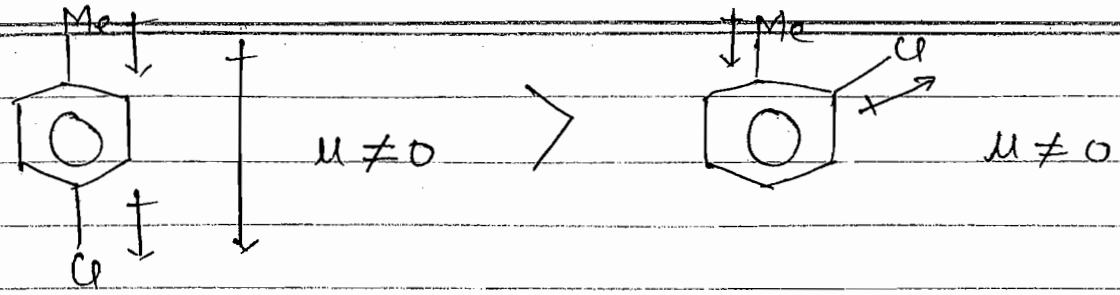
ortho $\vec{\mu} \neq 0$ $\theta = 60$

meta $\vec{\mu} \neq 0$ $\theta = 120$

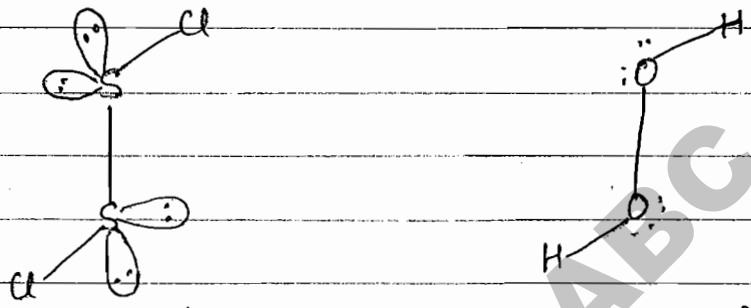
para.

$\mu \propto \frac{1}{\sqrt{\theta}}$

$\mu_{ortho} > \mu_{meta} > \mu_{para}$

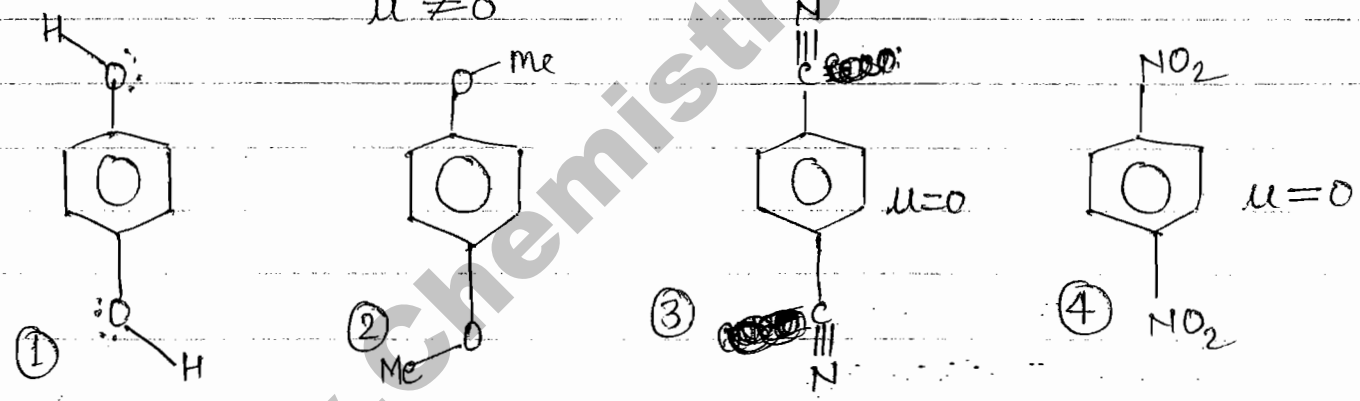


* S_2Cl_2



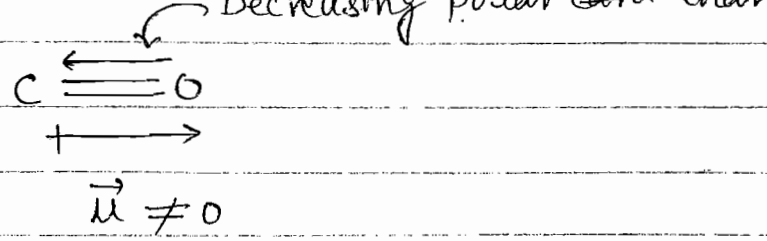
Open Book like str. (always $\mu \neq 0$)

$\mu \neq 0$

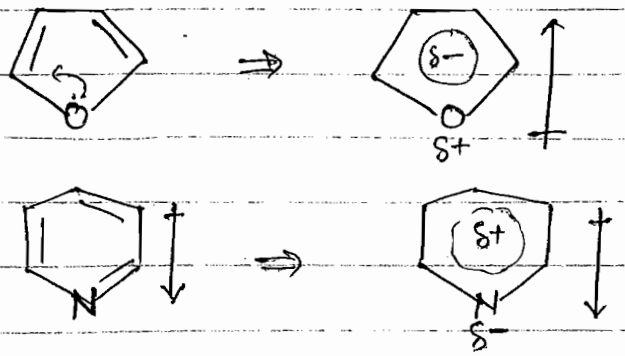


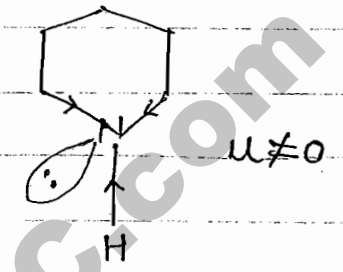
①, ② All these are open book like ($\vec{\mu} \neq 0$)

* CO must be more polar but it is less polar due to $\mu_{substration}$. (Co-ordinate bond decreases polarity).

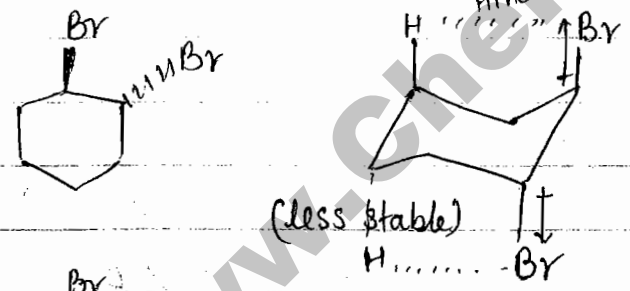


$\vec{\mu} \neq 0$



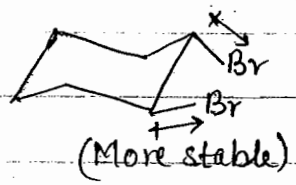


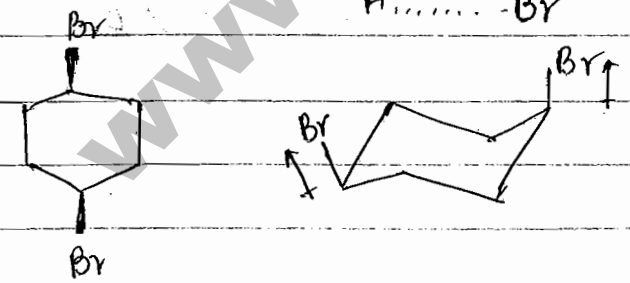
$\vec{\mu} \neq 0$



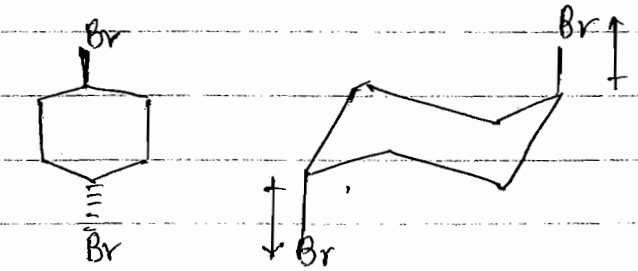
$\vec{\mu} \neq 0$ (Very low μ)

Both are not in same plane.



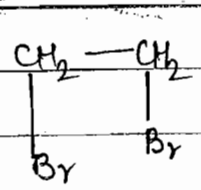


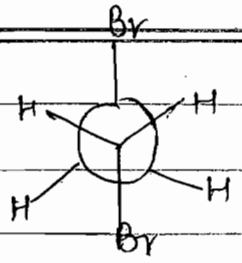
$\vec{\mu} \neq 0$

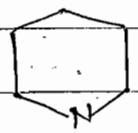
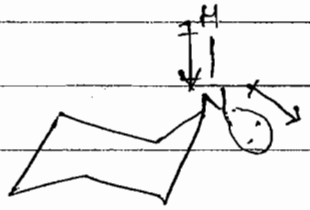


$\vec{\mu} \neq 0$

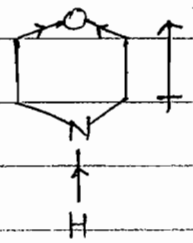
Very low dipole moment

*  $\vec{\mu} \simeq 0$



*  ⇒  (or) 

More Stable ⋔ Less stable

*  $\mu \neq 0$

Exception :- * $CH_3Cl > CH_2Cl_2 > CHCl_3$

μ increasing ←

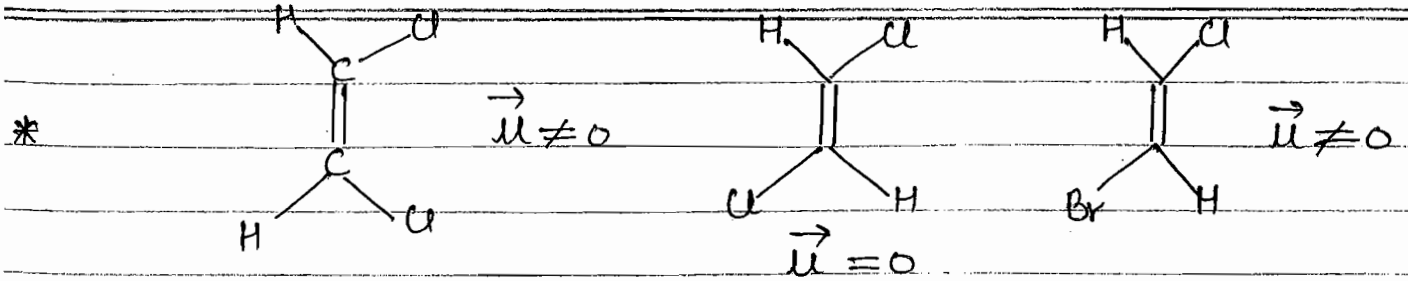
* $CH_3-F < CH_3-Cl$ (Bond length factor)

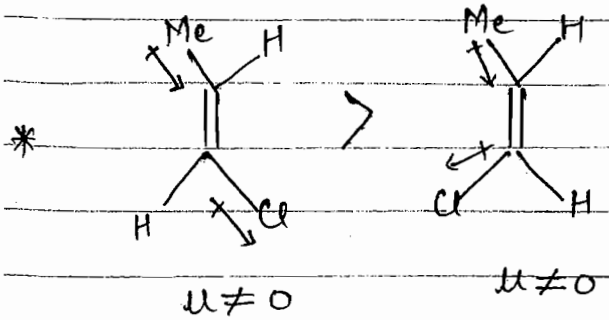
* $CH_3F < CH_2F_2 < CHF_3$

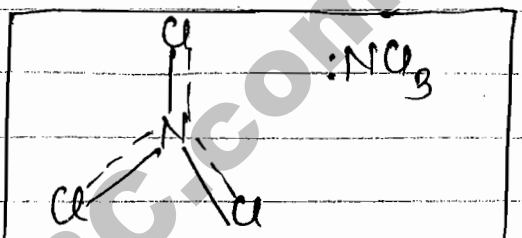
* $CH_2Cl_2 < CH_2F_2$

* $CHCl_3 < CHF_3$

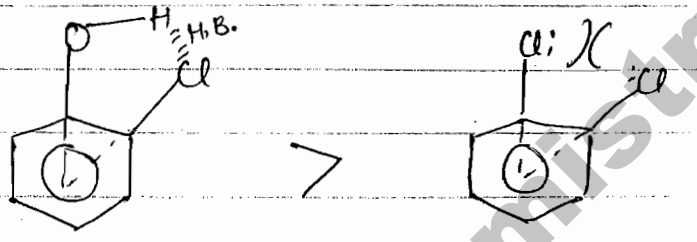
* $C_2H_5F > C_2H_5Cl$







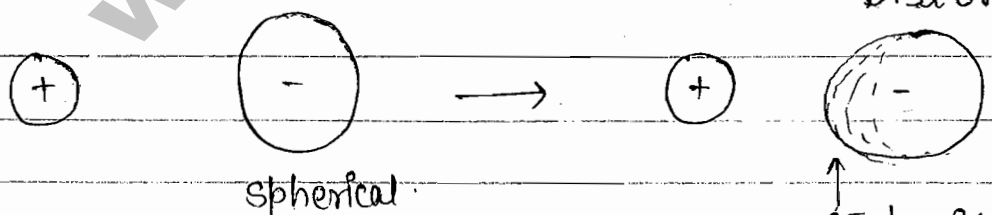
l.p. of 'N' delocalised into the vacant orb. of 'Cl' ⇒ Planar mol ⇒ $\mu = 0$



θ decreases due to H.B.

θ increases due to lp-lp repulsion

POLARISATION



Spherical

Distortion in shape

e⁻ density polarised due to ~~cat~~ induction of cation.

⇒ More polarisation; more will be co-valent character.

Fajan Rule

Cation	Anion.
* Attracting factor (Polarising power) P.P.	* Loosing factor (Polarisability) P.Z.

* ① $P.P. \propto \frac{1}{\text{Size(Cation)}}$

② * $P.P. \propto$ Charge of Cation.

③ * $Pz \propto$ Size of anion

④ * $Pz \propto$ Charge on anion

⑤ Cation → Noble gas config. ($8e^-$) eg. Na^+ (2,8)

→ Pseudo Noble gas config. (18,32) eg Cu^+ (2,8,18)

P.P. of Pseudo Noble gas config. > P.P. of Noble gas config.

⑥ $CuSO_4 > CuSO_4 \cdot H_2O$.

* Anhydrated cation more P.P. than Hydrated cation.
* H_2O causes hinderance in polarisation.

APPLICATION OF POLARISATION :-

Covalent character in ionic comp. $\propto$ Polarisation.

Usually covalent mol. has less solubility in water, (lower m.p. & lower b.p.)

Thermal Stability:-

$BeCO_3$
$MgCO_3$
$CaCO_3$
$SrCO_3$
$BaCO_3$

T.S. ↓ (size of cation increases)

$CaCO_3 \xrightarrow{\Delta} CaO + O_2$

Decomposition.

Temp. → Low (Thermally less stable)

Temp. → High (Thermally more stable)

* $LiNO_3 < NaNO_3 < KNO_3$

Thermal stability. →

Anion

Smaller ← Bigger

X^-, O^{--}, N^{---}

T.S. Top to Bottom decreases. ↑

CO_3^{--}, SO_4^{--}, OH^-, NO_3^-

CH_3COO^-, CrO_4^-, CrO_4^{--}

$Cr_2O_7^{--}$, MnO_4^-

T.S. Top to Bottom Increases. ↓

* Li_3N
Na_3N
K_3N

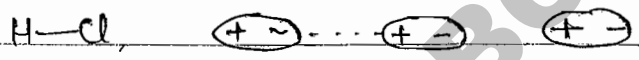
T.S. Decreasing. ↓

* Thermal Stability also depend on crystal arrangement. more the close packing, more will be thermal stability.

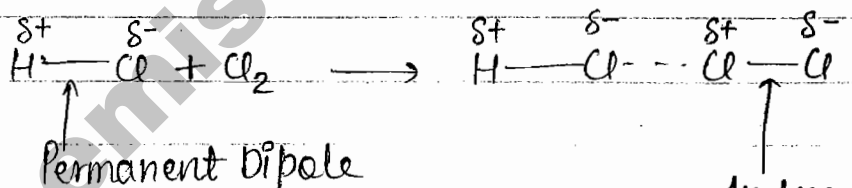
VANDERWAL FORCES:-

These forces are actually combination of diff. kinds of interaction, depending upon type of spp. Basically these are supposed to be a combination of three forces

i) Keeson Forces. **Dipole - Dipole interaction**



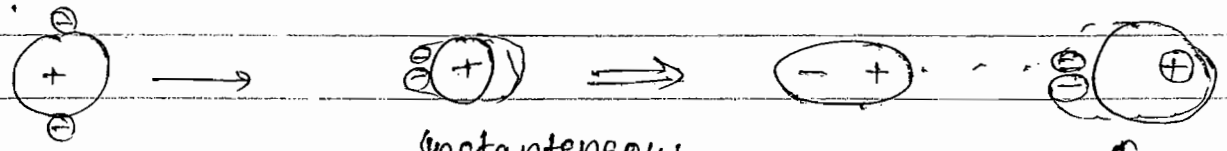
ii) Debye Forces:- **Permanent Dipole - induced dipole interaction**



Main Vanderwaal force

iii) London forces: **Instantaneous dipole - induced dipole interaction.**

Nonpolar H_2, Cl_2, He, Ne - - -



Factors affecting V.W.F.

VWF ∝ surface area.

VWF ∝ size

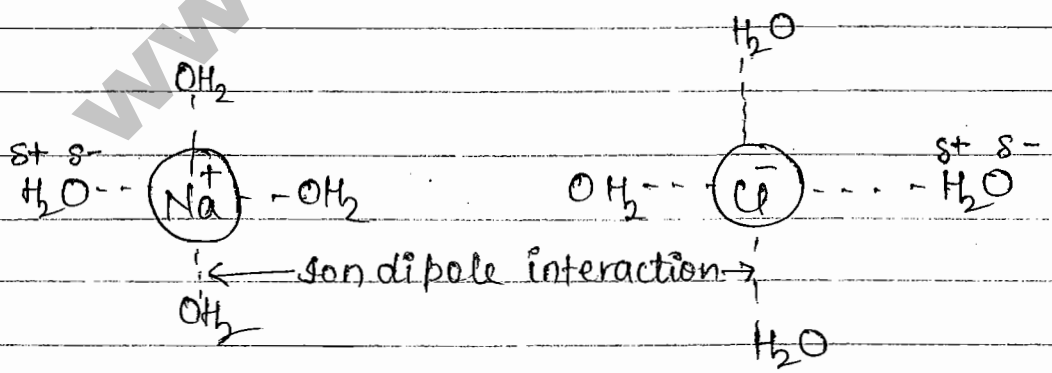
VWF ∝ No. of e⁻s

VWF ∝ Mol. mass

Forces

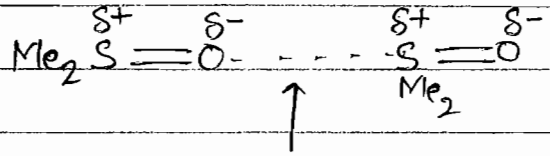
- chemical forces
  - Ionic Bond
  - Covalent "
  - Metallic "
  - Dative " (or) Co-ordinate
- Physical forces.
  - H-bond.
  - VWF

* $H_2O + NaCl \longrightarrow$



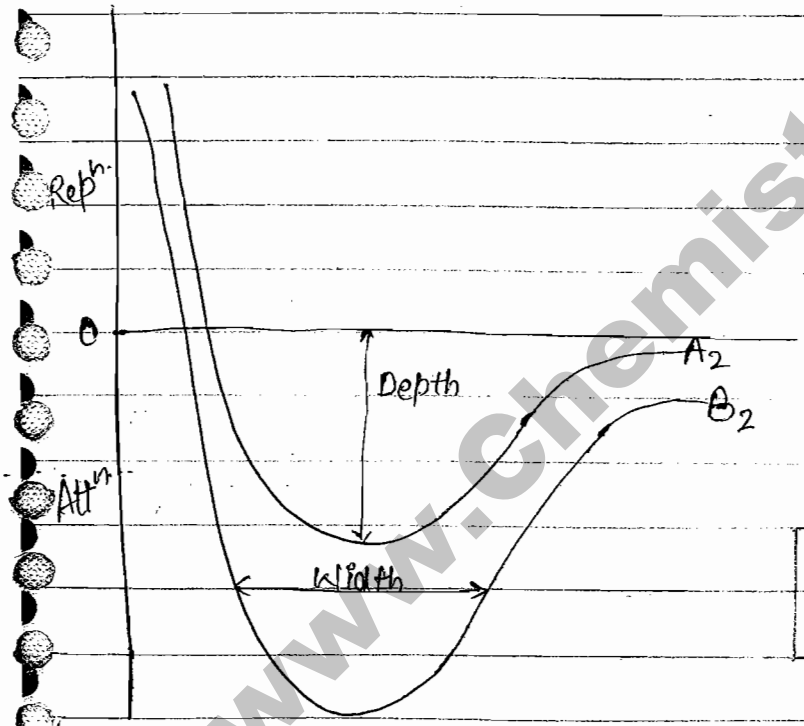
#Vander waal forces are molecular forces.

* DMSO (Polar liquid)



Dipole - Dipole interaction.

Leenard - Joneson Graph:-



depth denotes stability
Width denotes Bond Length.

Depth ∝ Stability

Width ∝ Bond length.

$$E_T = \frac{A}{r^6} + \frac{B}{r^n}$$

Type of interaction	Bond distance.
Ionic bond	$\propto \frac{1}{r_1}$
Ion-dipole interaction	$\propto \frac{1}{r_2}$
Dipole - Dipole	$\propto \frac{1}{r_3}$

Ion induced dipole $\propto \frac{1}{r^4}$

dipole " " }
Instantaneous dipole - induced dipole } $\propto \frac{1}{r^6}$

Order of bond Strength

Ionic > Metallic > co-valent ✗ H-bond ✗ VWF.

H-Bonding is a kind of dipole-dipole interaction (VWF)

$H_2O \cdots H_2O$
$H_2S \cdots H_2S$
} Nature of bonding (interaction same) i.e. dipole-dipole interaction but magnitude different.

Application of VWF:-

Q. H_2, D_2, T_2 B.P. ?

H_2, D_2, T_2

Mass increases.

More VWF ⇒ More B.P.

VWF ∝ mass

H-Bonding

* B.P. $HF > \underline{HI > HBr > HCl}$
Acc. to VWF.

* $H_2O > H_2Te > H_2Se > H_2S$
↑ H-Bond. Acc. to VWF

* NH_3] H-Bonding
PH_3, AsH_3 } VWF < H-Bonding of NH_3
SbH_3, BiH_3 } VWF > Hydrogen bonding of NH_3

Now order of B.P. will be - $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

* $PbH_4 > SnH_4 > GeH_4 > SiH_4 > CH_4$

* B.P. $SO_3 > SO_2$
↑ More Mol. mass.

* B.P. ⇒ B.P. don't depends upon crystal str. & Packing

* M.P. ⇒ M.P. " " " " "

λ ⇒ small lambda Λ ⇒ capital lambda.

Boiling Point ∝ Molecular Mass.

* Melting Point $C_6 > C_7$

* M.P. of Odd Carbon < M.P. of even Carbon. (Carbon diff. should be one).

M.Sc.

Electronic Spectra of Diatomic Spp.:-

Term Symbol:-

Procedure

Homodiatomic Molecules

① Write the molecular configuration.

$\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$ - - - - -

(or)

σg^2, σu^2, σg^2 σu^2 - - - - -

② Find Last energy M.O.

③ Find Spin Multiplicity (m) = $2S+1$

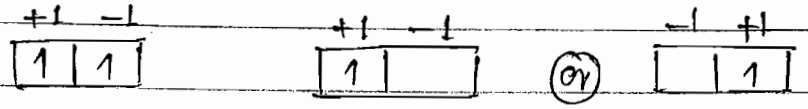
↑ Total spin.

L ⇒ Never be -ve.

σ	Σ
π	Π
α	Δ
β	Φ
γ	Γ
λ	Λ
φ	ϕ
θ	(H)
k	K

m → 1 Singlet state
m → 2 Doublet state
m → 3 Triplete state
. . . . . .

④ Find Σl or L or Λ or Σml or Total Angular Q. No.



L = +1 −1 = 0 L = +1 (or) L = +1

Note- 'L' should be ~~zero~~ ~~and~~ positive.

L	Term
0	Σ
1	Π
2	Δ
3	Φ
. . .	. . .

⑤ Write g & u

Eg. Π_{2p_x} Π_{2p_y}

↑ ↑
u u

g × g → g
u × u → g
u × g → u
g × u → u

} If both orbitals are filled.

Note: If only one orb. filled then write g/u acc. to that orb.

(c) In case of Σ term assign + & - sign

If M.O. is σ → (+)

If M.O. is π

- If $(2S+1) = 3$ → (−)
- If $(2S+1) = 1$ → (+)

Ex. $H_2 \Rightarrow \sigma 1s^2$

(or)

σg^2

$\uparrow\downarrow$

$m = 2S+1$

$= 1$

$l = 0$

$L = 0 \Rightarrow \Sigma$

$(2S+1)\Sigma$

spin multiplicity

1 → + ← ---- if σ (in mol. configuration) then '+'

L → g ←

Ex. $He_2^{\oplus}$ σs^2 $\sigma^* 1s^1$

(or) $\sigma g^2, \sigma_u^1$

$\sigma^* 1s^1$ (or) σ_u [1]

$m = 2S+1$

$= 2$

$L = 0 \Rightarrow \Sigma$

$^2\Sigma_u^+ \longleftarrow$ M.O. is 'g'

Ex. O_2 $\sigma 1s^2\ \sigma^* 2s^2,\ \sigma 2s^2,\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^*_{2p_x}{}^1\ \pi^*_{2p_y}{}^1$

$\sigma_g^2\ \sigma_u^2\ \sigma_g^2\ \sigma_u^2\ \sigma_g^2\ \pi_u^4\ (\pi_g^2)$

π_g^2

+1	−1
1	1
g	g

(or)

+1	−1
1↿	
g	g

(or)

+1	−1
1	1↿
g	g

$m = 3$ $\quad$ $m = 1$ $\quad$ $m = 1$

$L = 0 \Rightarrow \Sigma$ $\quad$ $L = 2 \Rightarrow \Delta$ $\quad$ $L = 0 \Rightarrow \Sigma$

$^3\Sigma_g^-$ ($m=3$) ← G.S.T. ; $g \times g = g$

$^1\Delta_g$ — Ist Excited Term

$^1\Sigma_g^+$ ($m=1$) — IInd Excited Term.

* Ground state term $\Rightarrow$ Max. $(2S+1)$ & max. 'L' value. (if $(2S+1)$ same for all terms)

Hund Rule for Term Symbol Selection.

* For stable term $m=(2S+1)$ should be high.
* " " " Value of 'L' should be high.

Note:- To decide G.T. firstly check $(2S+1)$ ⇒ spin multiplicity, if $(2S+L)$ same then check the max. value of 'L'.

Ex. O_2^+ $\sigma 1s^2$ $\sigma^* 1s^2$ $\sigma 2s^2$ $\sigma^* 2s^2$ $\sigma 2p_z^2$ $\pi 2p_x^2$ $\pi^* 2p_x^1$
$\pi 2p_y^2$ $\pi^* 2p_y$

π_g^1

π_g^1

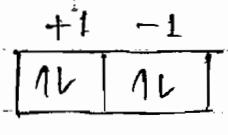
$L = 1 \Rightarrow \Pi$

$(2S+1) = 2$

$^2\Pi_g$

Ex O_2^{--}

$\pi^* 2p_x^2$
$\pi^* 2p_y^2$
π_g^4



π_g^4

$L = 0 \Rightarrow \Sigma$

$(2S+1) = 1$

$^1\Sigma_g$

TA. Imp.

Selection Rule for electronic transition in diatomic molecules.

1) Spin Selection Rule.

$\Delta S = 0$ (spin multiplicity constant) $\Rightarrow$ Allowed ✓

$\Delta S \neq 0$ (" " change) $\Rightarrow$ Forbidden.

2) Laporte Selection Rule.

$\Delta l = 0$ or ± 1 allowed. ✓

$\Delta l = \pm 2, \pm 3, \ldots$ etc. Forbidden

$\Sigma \longrightarrow \Sigma$ ✓ $\quad \Sigma \longrightarrow \pi$ ✓ $\quad \Sigma \longrightarrow \Delta$ X

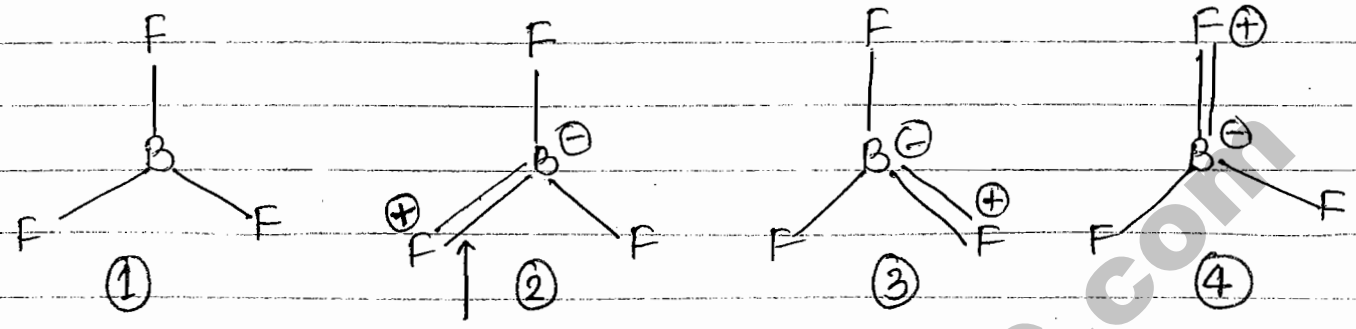
3) Parity Rule.

$g \longrightarrow g$, $u \longrightarrow u$ } Forbidden.

$g \longrightarrow u$, $u \longrightarrow g$ } Allowed

Allowed Transitions.
$\Delta S = 0$
$\Delta l = 0$ or ± 1
$g \longrightarrow u$
$u \longrightarrow g$
$+ \longrightarrow +$
$- \longrightarrow -$

BACK - BONDING



Back Bonding ($2p_\pi - 2p_\pi$)

Stability

$$\underbrace{② = ③ = ④}_{\text{octet complete}} > \underbrace{①}_{\text{No Octet complete}}$$

* BF_3 $2p_\pi - 2p_\pi$

BCl_3 $2p_\pi - 3p_\pi$

BBr_3 $2p_\pi - 4p_\pi$

BI_3 $2p_\pi - 5p_\pi$

↑ Lewis acidity Decreasing

↓ Back bonding decreasing

↓ Bond order Decreasing

* $B + F_2 \xrightarrow{K_1} BF_3$

$B + Cl_2 \xrightarrow{K_2} BCl_3$

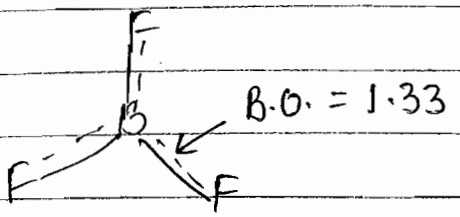
$B + Br_2 \xrightarrow{K_3} BBr_3$

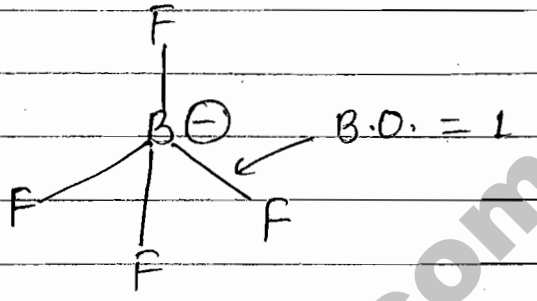
$B + I_2 \xrightarrow{K_4} BI_3$

$K_1 > K_2 > K_3 > K_4$

Arrhenius & Bronsted acid stronger acid than lewis acid. (84)

Q B-F Bond length in BF_3 & $B\bar{F}_4$





B-F Bond length BF_3 < B-F bond length $B\bar{F}_4$

* $\overset{+}{Na}\,\overset{-}{B}F_4$ — More thermal stable (ionic) 8 e^- on Boron

BF_3 — Less thermal stable (covalent) even B.O. of BF_3 is 1.33 which is more than $B\bar{F}_4$ (B.O. = 1).

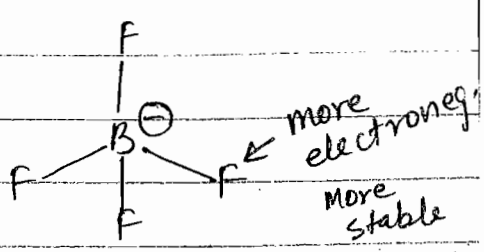
* $\overset{+}{Na}\,\overset{-}{B}(OH)_4$ — More stable

$B(OH)_3$ — less stable (covalent)

Q $H[\overset{8e^-}{BF_4}]$ (I), $\overset{6e^-}{BF_3}$ (II), $H[\overset{8e^-}{B(OH)_4}]$ (III) acidic strength. ?

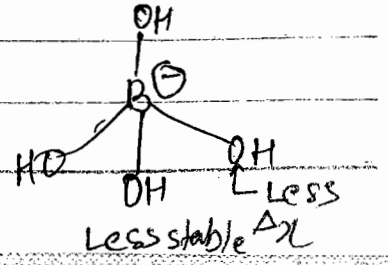
$H(BF_4) \rightleftharpoons \bar{B}F_4 + H^{\oplus}$

conj Base.



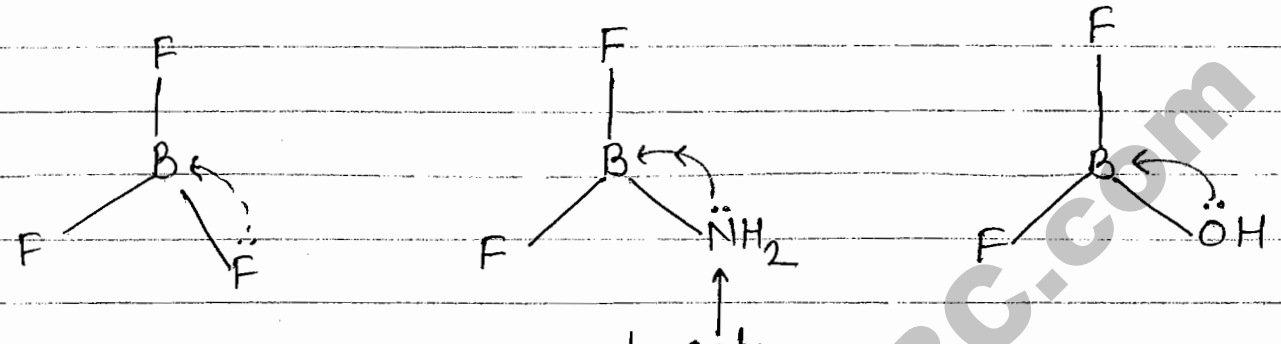
$H[B(OH)_4] \rightleftharpoons H^{\oplus} + \bar{B}(OH)_4$

conj Base.



Order of acidity I > III > II

Q BF_3 (I) BF_2NH_2 (II) BF_2OH (III) acid strength.



Least electronegative

⇓

More Back donation

⇓

Weakest L. Acid.

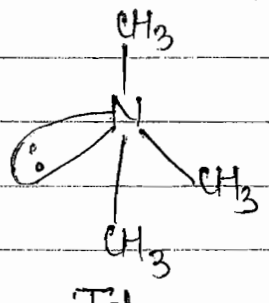
Order of Back Bonding: II > III > I

Order of acidity ⟶

Q. Basicity $\ddot{N}(CH_3)_3$, $\ddot{N}(SiH_3)_3$?

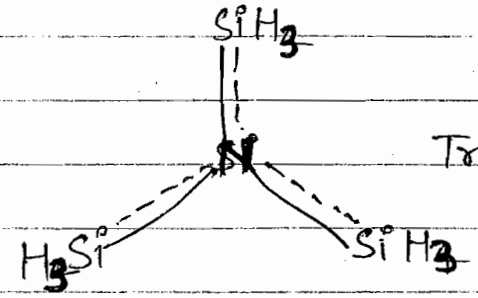
$\ddot{N}(CH_3)_3$: No vacant orb.

$\ddot{N}(SiH_3)_3$: vacant orb.



Tet.

More basic



Trigonal Planar

B.O. = 1.33

* $\ddot{N}(CH_3)_3$ No. Back Bonding

$\ddot{N}(SiH_3)_3$ Back Bonding 2p - 3d

$\ddot{N}(GeH_3)_3$ 2p - 4d.

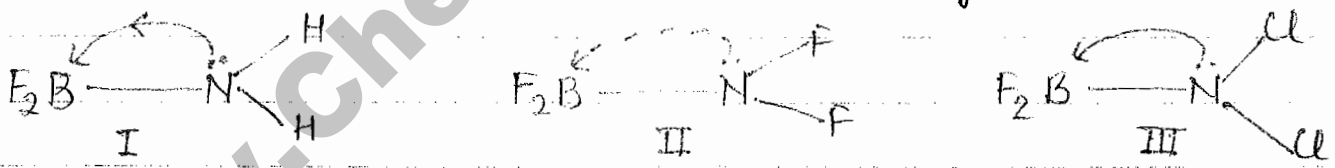
$\ddot{N}(SnH_3)_3$ 2p - 5d.

Lewis Basic strength.

$N(CH_3)_3 > N(GeH_3)_3 > N(SnH_3)_3 > N(SiH_3)$

Less back donation but more steric crowding

B.B.

Q. 

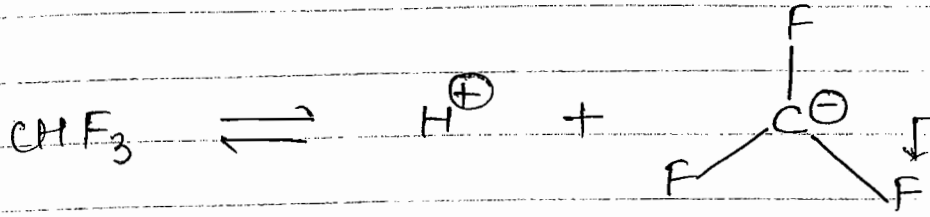
arrange the order of Rotational Energy barrier for B—N bond.

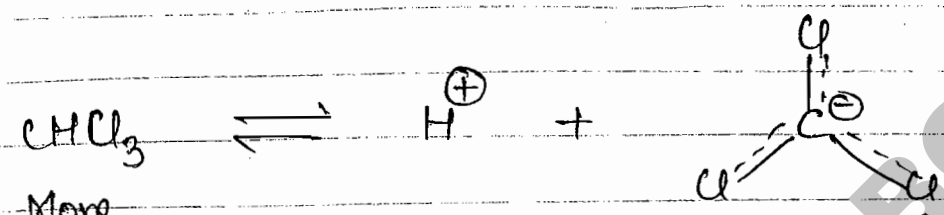
(I) More back donation ⇒ B.O. more ⇒ More energy to rotate B—N bond.

(II) Less back donation ⇒ Less B.O. ⇒ Less energy require to rotate B—N bond.

Order will be - I > III > II

Q. CHF_3 , $CHCl_3$ acidity ?



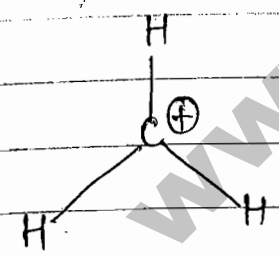


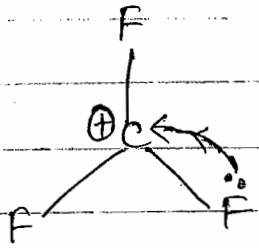
More acidic

More stable C.B.

Back donation

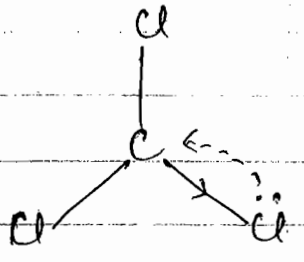
Q Stability $\overset{\oplus}{C}H_3$, $\overset{\oplus}{C}F_3$, $\overset{\oplus}{C}Cl_3$?





2p - 2p

Back bonding

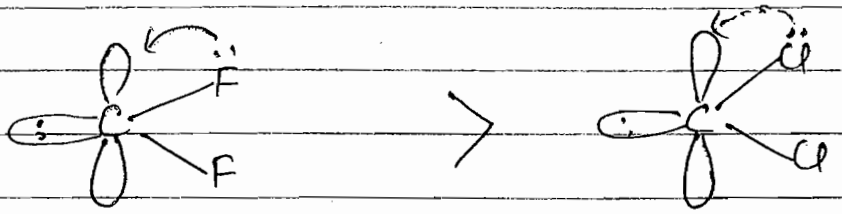


-I Effect dominant on Back bonding

Stability order $\overset{\oplus}{C}F_3 > \overset{\oplus}{C}H_3 > \overset{\oplus}{C}Cl_3$

If 'B' & 'Si' atoms / e^- deficient centre with adjacent atom having l.p. ⇒ Back donation possible.

Q $:CF_2$, $:CCl_2$ stability ?

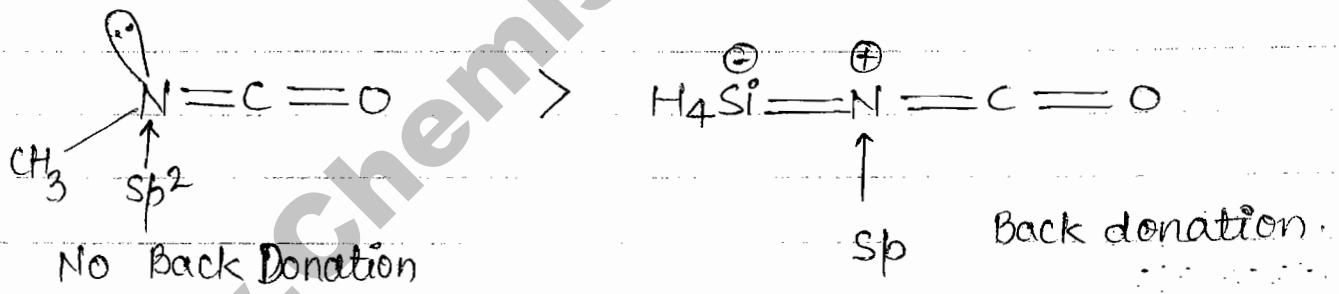


2p-2p Back donation.

2p-3p Back donation.

Imp.

Q. $CH_3-N=C=O$, $H_3Si-N=C=O$ Basicity ?



No Back Donation

Back donation.

Lattice Energy :-

Amount of energy released when one mole of ionic solid is form from it's constituent gaseous ions. Lattice energy is always released due to attraction b/w ions.

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$ $\quad -\Delta H$ ↑ Lattice Energy

$-U$

$$\underset{(s)}{Na^{+}Cl^{-}} \xrightarrow[+\Delta H]{\Delta} \underset{(g)}{Na^{\oplus}} + \underset{(g)}{Cl^{\ominus}}$$

Stability $\propto$ Lattice Energy

Measurment of Lattice energy

Theoretical ⟷ Experimental.

⇓

① Born Lande Eqⁿ

$$U = -\frac{N_0 |Z_+ \cdot Z_-| e^2}{r_0}\left[1 - \frac{1}{n}\right]$$

N_0 = Avagadro Number, Z_+, Z_- = Charge

$r_0 = r_+ + r_-$, e = charge of e^-

n = Born exponent diff.

A = Madulung constant.

System	n
He	5
Ne	7
Ar	9
Kr	10
Xe	12

Q Find 'n' for NaCl

$\overset{\oplus}{Na}$	$\overset{\ominus}{Cl}$
2, 8	2, 8, 8
[Ne]	(Ar)
7	9

$$n = \frac{7+9}{2} = 8$$

$\boxed{n = 8}$

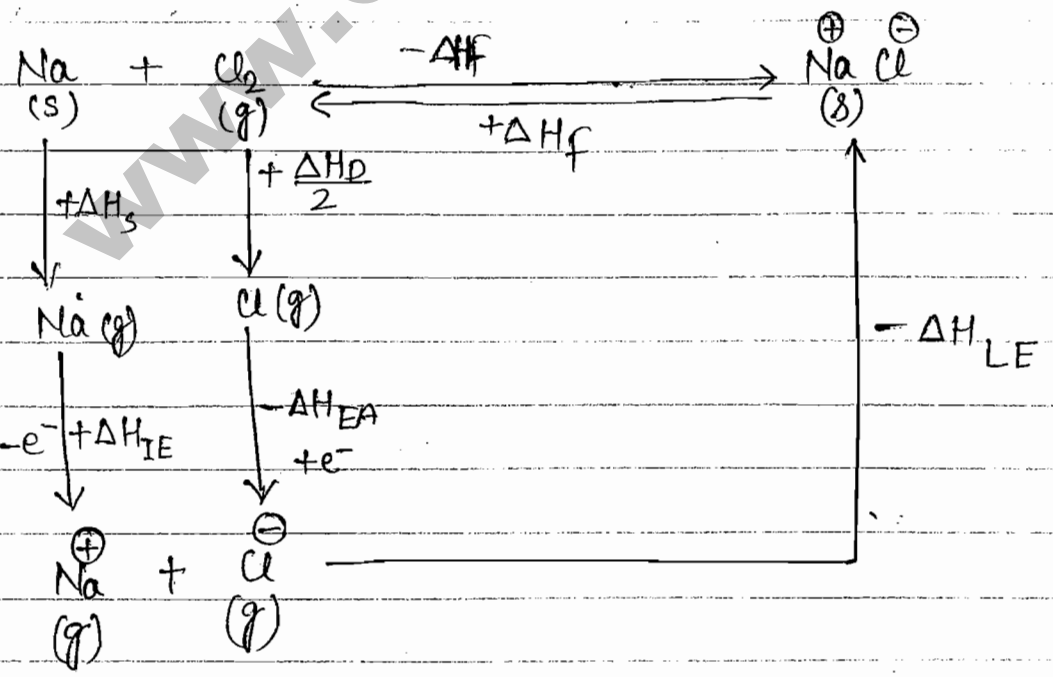
② Kapustinskii eqn:-

$$U = n\,\frac{[Z_+ \cdot Z_-]}{d}\left[1 - \frac{d}{d_0}\right]_{ion} A$$

n = no. of ions / formula unit.

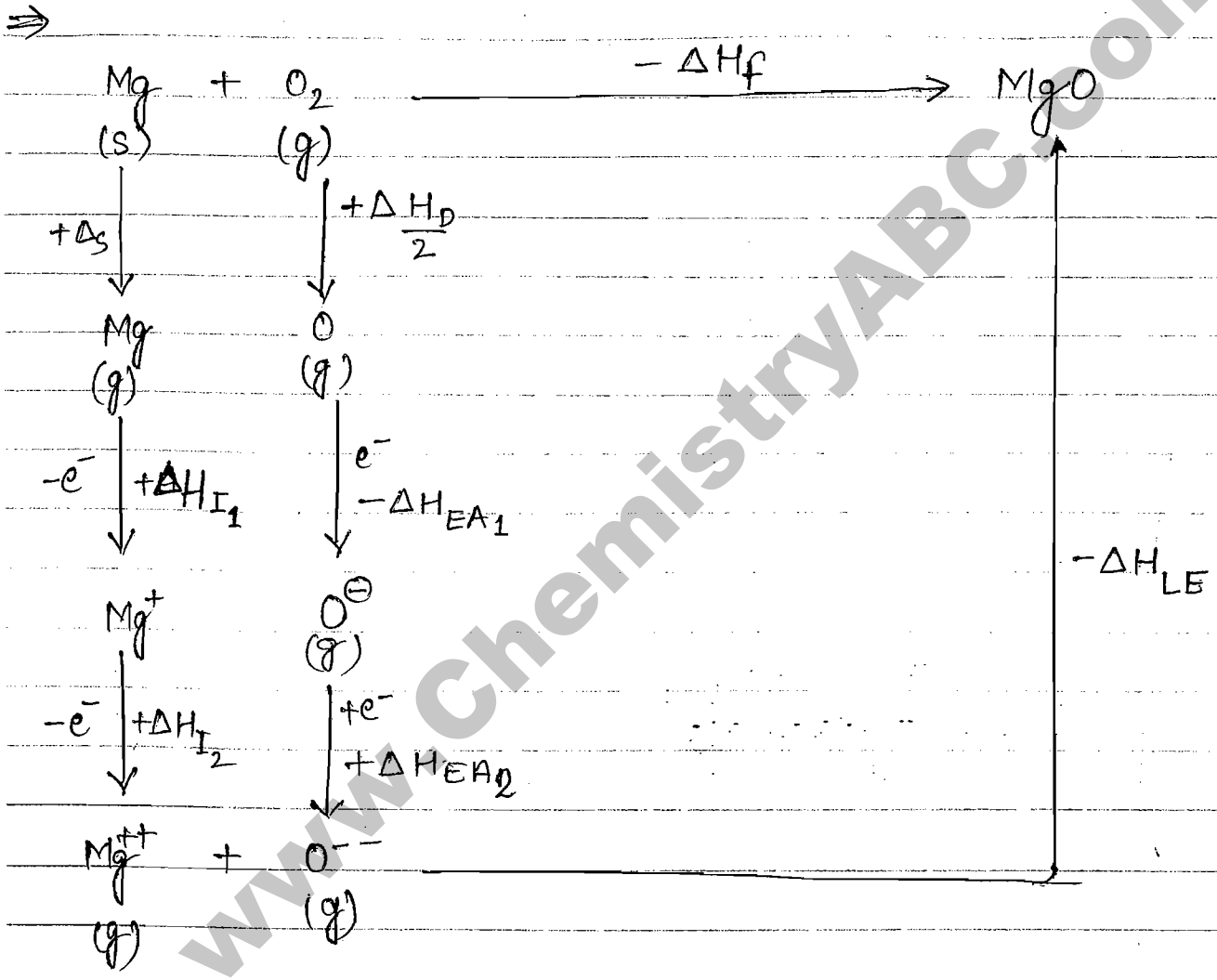
$A = 1.21 \times 10^5$ K.J./mole

Born Haber Cycle :-



Acc. to Hess's Law

$$-\Delta H_f = +\Delta H_S + \Delta H_{IE} + \frac{\Delta H_D}{2} - \Delta H_{EA} - \Delta H_{LE}$$



छोटे - छोटे (or) बड़े - बड़े ions ⇒ Good Packing
छोटे - बड़े (or) बड़े - छोटे ions ⇒ Not good Packing.

Factor Affecting L.E.

Lattice Energy ∝ Charge

$$L.E \propto \frac{1}{\text{Bond length}}$$

L.E ∝ force of Attraction.

L.E. ∝ A (Meduleng factor)

L.E. ∝ Packing fraction.

* L.E ⇒ formation Energy
  H.E. ⇒ Breaking Energy
  ⇓
  Hydration Energy.

* L.E. > H.E. ⇒ Insoluble

  L.E. < H.E. ⇒ Soluble

  L.E. = H.E. ⇒ sparingly soluble almost insoluble.

⇒ H.E. & L.E. Both decreases from top to bottom in gp. but decrease in H.E. is more than decrease in L.E. therefore normally on going top to bottom solubility generally decreases.

Abnormal Behaviour of Salt:-

In first gp: ⌗ F^-, $\bar{O}H$, Oxalate show abnormal char.

In II gp. f^-, $\bar{O}H$, $\bar{C}\bar{O}_3$ show abnormal char.

Q. Arrange L.E. NaCl, $MgCl_2$, $AlCl_3$

Na^+Cl^- $Mg^{2+}Cl^-$ $Al^{3+}Cl_3^-$

$\longrightarrow$

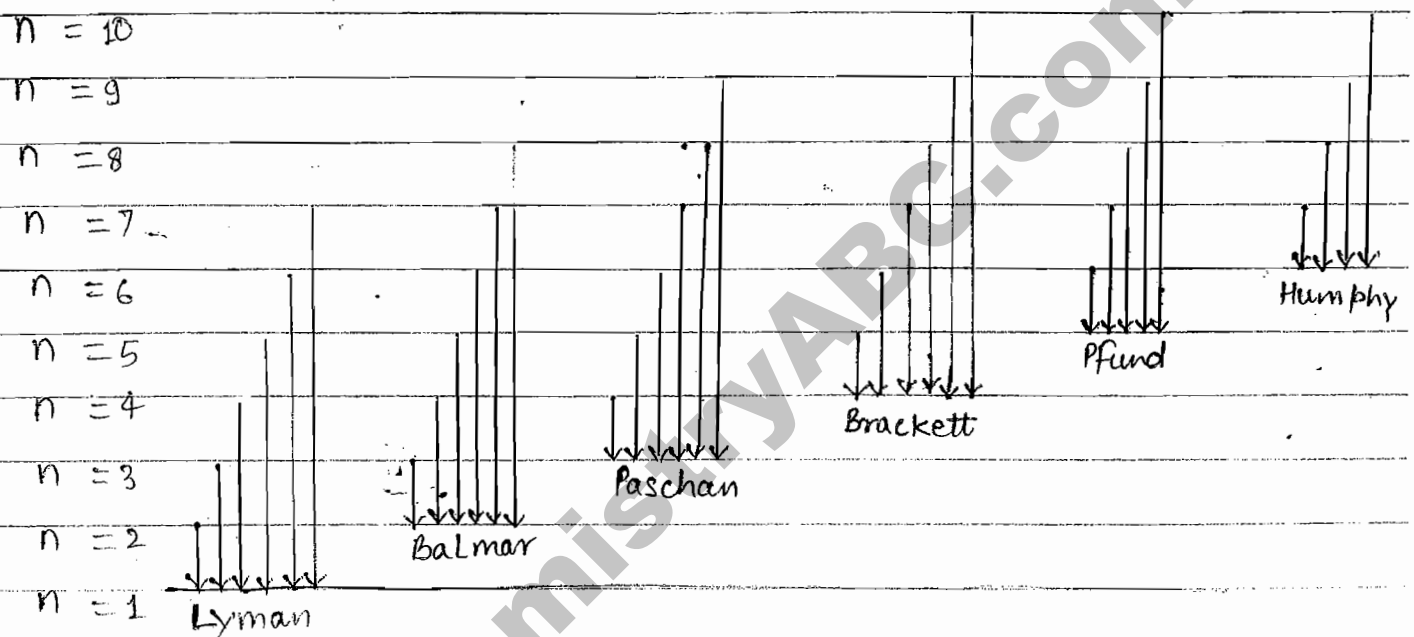
Size of cation decreases. i.e.

more close ions $\Rightarrow$ L.E. increases.

14/08/2014

ATOMIC STRUCTURE

Atomic Spectra of 'H' / Emission Spectrum:-



n = Shell of Hydrogen.

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$\bar{\nu}$: Wave No.

R_H : Rydberg const. $= 109678\ cm^{-1}$

Z : At. No.

n_1 = Ground state

n_2 = Excited state

* No. of lines, when n_1 & n_2 are given,—

$$\boxed{\text{No. of lines} = \Sigma \Delta n}$$

$$\hookrightarrow \Sigma (n_2 - n_1)$$

Eg. From 5 to 1, no. of lines.?

n_2 n_1

No. of lines. $= \Sigma \Delta n$

$= \Sigma (5-1)$

$= \Sigma 4$

$= 4+3+2+1$

$= 10$ lines

* No. of fine lines $= n_1 \times n_2$

Eg No. of fine lines if 5 to 1 ?

No. of fine lines $= n_1 \times n_2 = 5 \times 1 = 1$

* Max. no. of emission lines when e^- jump from nth shell to ground state. $= \frac{n(n-1)}{2}$

Eg. if $n = 5$.

$\Rightarrow \frac{5(5-1)}{2} = 10$

Bohr Theory :- First Quantised Model

$$r = 0.529 \frac{n^2}{Z} \text{ A}^\circ$$

$$E = -13.6 \cdot \frac{Z^2}{n^2} \text{ eV/atom}$$

Z = At. No.
n = shell

$$v = \frac{2\pi e^2 Z}{h \cdot n}$$

$$\text{Angular momentum} = \frac{h}{2\pi}\sqrt{l(l+1)}$$

Radial Probability Distribution Curve (on the basis of Schrodinger Wave Eqn.) :-

$$\nabla^2\psi + \frac{8\pi^2}{h^2} m [E-V] = 0$$

de broglie eqn.

$$E = mc^2$$

$$E = h\nu$$

$$mc^2 = h\nu \Rightarrow mc = \frac{h\nu}{c} \Rightarrow mc = \frac{h\nu}{\nu\lambda}$$

$$mc = \frac{h}{\lambda}$$

$$mc = p = \frac{h}{\lambda}$$

Heisenberg Uncertainity Principle.

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

$$\frac{h}{2\pi} = \hbar$$

↑ h-Cross

$P = mv$

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta (mv) \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

$$\boxed{\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}}$$

$$\boxed{\Delta E \times \Delta t \geq \frac{h}{4\pi}}$$

On the basis of Heisenberg's Principal. If e^- is present inside the nucleus then its velocity will be greater than that of sunlight, which is impossible.

Radial probability curves are the graph b/w radial probable volume (f_r) and r (distance from nucleus).

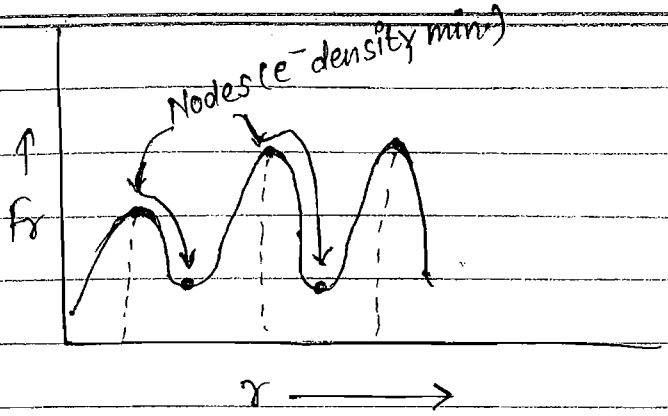
$$\boxed{\int_{r=r}^{r=0} f_r = 4\pi r^2 R^2_{n,l} \, dr}$$

$R^2_{n,l}$ ← Radial Probability

6] 4, 6 C.N.

4. C.N. of P

5 C.N.

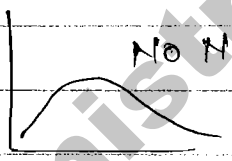


Nucleus.

M.Imp.

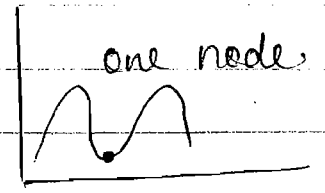
No. of Radial Nodes = n − l − 1

Eg. 1s Radial Node = 1 + 0 − 1 = 0



$eH_3)_2$

2s R. Node = 2 − 0 − 1 = 1

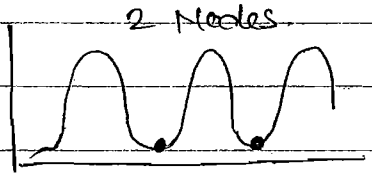


Me

1

ple

3s R. Node = 3 − 0 − 1 = 2



$\frac{12}{2}$ = 6 Steric No.

O⁻

O⁻ O O⁻

$\frac{6}{2}$ = 3 Steric No.

$P = mv$

Δx

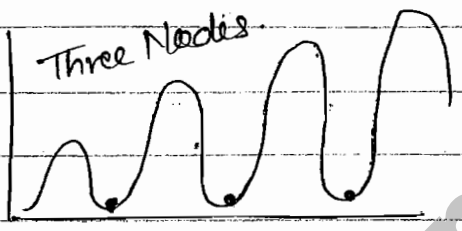
$\Delta x \cdot$

$\Delta x \cdot m$

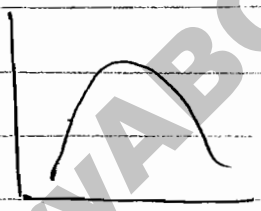
$\Delta x \cdot \Delta$

$\Delta E \times$

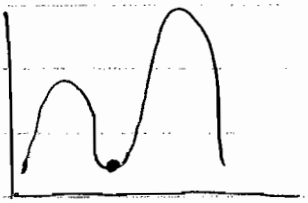
4S ⇒ R. Nodes = 4 − 0 − 1 = 3



2p ⇒ R. Node = 2 − 1 − 1 = 0



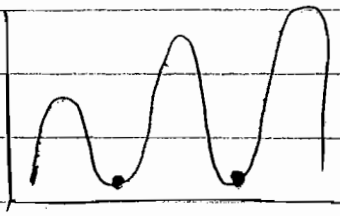
3p ⇒ R. Node = 3 − 1 − 1 = 1



On the basis of
is side the
greater than t

Ra
two radial
nucleus).

4p ⇒ R. Nodes = 4 − 1 − 1 = 2



$$\int_{r=r}^{r=0} f_r =$$

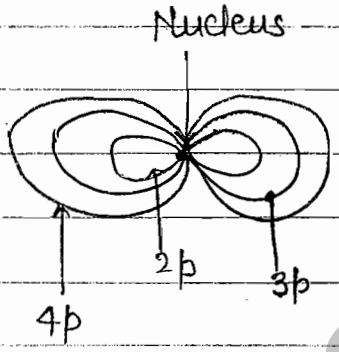
dumb-bell ∞

Solid $PCl_5 \Rightarrow [PCl_4]^+ [PCl_6]^-$ 4,6 C.N.

Solid $PBr_5 \Rightarrow [PBr_4]^+ Br^-$ 4. C.N. of P

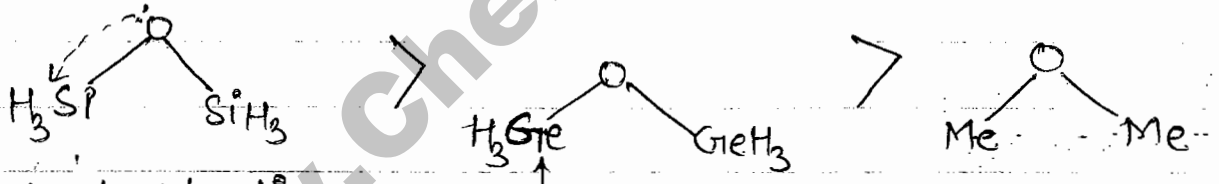
Gas $PCl_5 \Rightarrow PCl_5$ 5 C.N.

p- subshell representation around Nucleus.



* **No. of Angular Node = 'l'**

Q bond angle order OMe_2, $O(SiH_3)_2$, $O(GeH_3)_2$



due to π bonding angle increases.

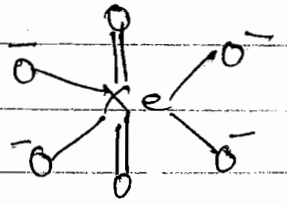
Big size (More repulsion)

⇓

More bond angle

Q Geometry of XeO_6^{4-}

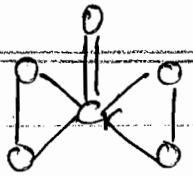
8 + 4 = 12 Steric No. $\frac{12}{2}$ = 6 Steric No.



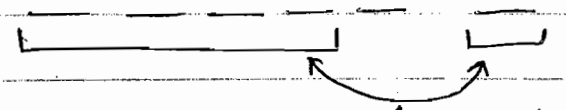
* SO_2

$\frac{6}{2}$ = 3 Steric No.

If two options are correct among four options in exam then choose most appropriate (correct) answer.

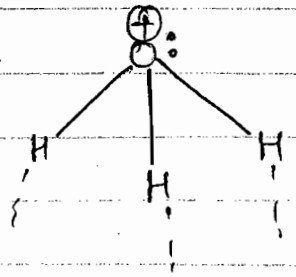
*  Butterfly

$Cr^{+6} = s^0 d^0 = sd^4$ $\quad d^0 \quad s^0$

$= d^0 s^0 \Rightarrow$ 

d^4s hybridisation

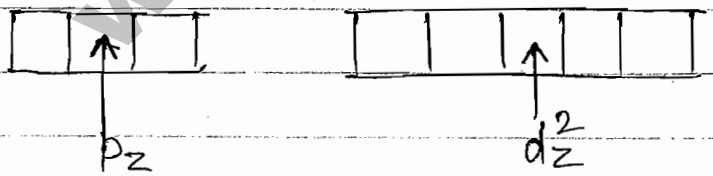
$\Rightarrow sd^4$ hybridization is more correct than d^4s hyb.

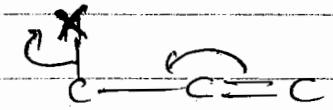
*  Pyramidal str.
3 H.B (Oxygen can't form H.B. $\Rightarrow$ +ve charge)

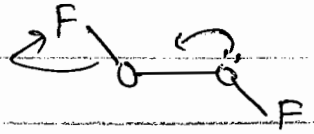
Thermal
* Stability order $LiO_3 < NaO_3 < KO_3$
छोटू-बड़ू बड़ू-बड़ू

* HF Geometry of F $\Rightarrow$ Td.
Highest occupied orb. is Non bonding.

* $n=3, l=1, m_l=0, m_s=+1/2 \Rightarrow 3p_x$



*  Hyper conj With halogens.

*  Hyper-conj by F

s	p	d	f	g	h	I	j	k
1	3	5	7	9	11	13	15	17
⇓								⇓
$2e^-$								$34e^-$

Zn is MGE $(3d^{10}, 4s^2, 4p^0, 4d^0)$

Cu, Ag, Au ⇒ Semi main group element

28/09/2014

MAIN GROUP ELEMENT

Those elements in which only one shell is incomplete are called M.G.E.

All shell complete ⇒ Nobel Gas Element.
18th group.

Only one incomplete shell ⇒ Main Group Element
s,p except 18th group

More than one incomplete shell ⇒ Transition Metal Element .d & f.

Q. Which is not a main group element ?
i) Na ii) Zn iii) K iv) Fe

Na 2, 8, 1
Cl 2, 8, 7
✓ Fe 2, 8, 14, 2
Zn $3d^{10}$, $4s^2$, $4p^0$ ...

Group No. 12 Zn, Cd, Hg only one shell incomplete. ⇒ MGE

* La is d-block element becoz f orb. having no. any e⁻. $4f^0, 5d^2, 4s^2$

Incomplete shell ⇒ Valence Shell ⇒ shell that's e^- participate in bonding

s-BLOCK ELEMENT Alkali metals

I	II
H	He ← last e^- enters in s ⇒ $1s^2$
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra

Total element = 14

ns^1 ns^2

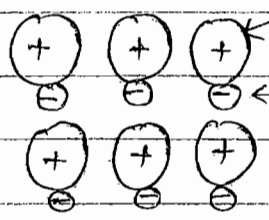
s-block	d-block
Metals.	Metals.
Soft	Hard.
Low m.p., b.p.	High m.p., b.p.
Low I.E.	High I.E.
Low density	High density
Light wt.	High wt.

weight

Metallic Bonding → Electron Sea/gas Model

$Na^+ + e^-$

Kernel ↑ Valence Electron.



s-block ⇒ only metallic bonding

d-block ⇒ Metallic as well as co-valent bonding i.e. why More density, m.p., b.p. etc.

Heat of Atomisation :-

Amount of heat needed to convert one gram mole metallic crystal into gaseous form.

*Heat of atomisation or Cohessive Energy similar in energy but sign opposite

Li - - - - - - - - - - Cs.

Cohessive Energy decreases →

Less C.E. ⇒ Less Hardness, m.p., b.p.

smp Due to less cohessive Energy Cs changes into liq. on rubbing on palm. (~28°C m.p.)

* Similar size atoms & similar Valence shell metals can form alloy.

* Li is miscible only with Na atom 350°C, but other atoms metals miscible with one another.

NET Q. Which miscibility pair is not correct.

✓a) Li/Rb b) Rb/Cs c) K/Rb d) K/Cs

Always second I.E. higher than first I.E.

I.E. Top to bottom decreases.

Low I.E of sblock becoz ∝ size is large

$$Ca \xrightarrow[I_1]{-e^-} Ca^+ \xrightarrow[I_2]{-e^-} Ca^{2+}$$

$Ca \xrightarrow{I_1} Ca^+ \Rightarrow Ca^+ X^{\ominus}$ Less stable.

$Ca \xrightarrow{I_1+I_2} Ca^{2+} \Rightarrow Ca^{2+} X_2^{\ominus}$ More stable i.e. why Ca^{2+} more easily form even more I.E. than Ca^+.

* Lowest amount of first I.E. of Cs in all the elements.
* Cs used in photoelectric doors.

FLAME COLOURATION :-

Li	Na	K	Rb	Cs
Crimson Red	Golden Yellow	Voilet		

* Bunsen burner ⇒ It produces Energy only for excitation e^- not for releasion from Metals.

Bunsen burner provide same excitation energy to all element therefore the loosely bonded e^- of Cs excited to much higher energy level hence releases more energy at the time of relaxation.

ऊपर वाला दिया करता है (Li) नीचे वाला ले लिया करता है (F)
God. Human.

In Bunsen burner these elements also form compounds.
Ex. LiOH.
This colour concept is used in qualitative analysis of alkali metals in flame photometery.

Electrochemical Series :- (E.C.S.)

E.C.S. ⇒ ऊपर वाला Metal Anode, नीचे वाला metal cathode.

Mobile phone battery ⇒ Li-ion as an anode.

---

e^- gaining ability $\propto E^\circ_{Red.}$

Metals

- Li – Al Strong electropositive.
- Al — H Moderetuly electropositive.
- H – – F Least "

↓ Reactivity decreases of metals but increases the non metals

$$\text{Metal}_{(s)} \longrightarrow M_g + \Delta H_1 \quad \text{Sublimation. E.}$$

$$M_g \longrightarrow M^+_g + e^- + \Delta H_2 \quad \text{I.E.}$$

$$M^+ + aq. \longrightarrow [M(aq)]^+ - \Delta H_3 \quad \text{H.E.}$$

$\therefore$ Net change $\Delta H = +\Delta H_1 + \Delta H_2 - \Delta H_3$

= Always –ve in case of Ist alkali group

Reactivity :- In gaseous state $Li < Na < K, Rb < Cs$

In aq. medium $Na < K < Rb < Cs < Li$

Reactions :-

Rxn. with air.

$$M \xrightarrow{O_2} \underset{\text{oxide}}{M_2O} \xrightarrow{O_2} \underset{\text{peroxide}}{M_2O_2} \xrightarrow{O_2} \underset{\text{super oxide}}{MO_2}$$

$M_2O \xrightarrow{H_2O}$; $M_2O_2 \xrightarrow{H_2O}$; $MO_2 \xrightarrow{H_2O}$

Water Vapours & CO_2 both are green house gaseous.

When more moisture in air ⇒ Low wt. (light air)

air = 28 wt | air + H_2O = $\frac{28+18}{2}$ = 23 ← less wt.

↓ ↓ ↓

MOH | MOH + H_2O_2 | MOH + H_2O_2 + O_2

↓ CO_2 | ↓ CO_2

M_2CO_3 | M_2CO_3

$Li \xrightarrow{air} Li_2O$ (major) + Li_2O_2 (minor)

$Na \longrightarrow Na_2O$ (minor) + Na_2O_2 (major) ← peroxide NET

K, Rb, Cs $\longrightarrow MO_2$ Super oxide mainly

* Li^+ + O^{--} $\longrightarrow$ Li_2O

छोटू छोटू

* Cs^+ + O_2^- $\longrightarrow$ CsO_2

बड़ू बड़ू Superoxide

Q. Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O — Thermal stability decreases. ↓

Q LiO_2
NaO_2
KO_2
RbO_2
CsO_2

Thermal Stability increases.

⇐ Super oxides

Q $Li(O_3)$ ← बहुत बड़ा
NaO_3
KO_3
RbO_3
CsO_3

Thermal Stability increases.

	O^{2-}	O_2^+	O_2^{2-}	O_2^-	O_2	O_3^-
	oxide	Oxygenyl	peroxide	superoxide		Ozonide
B.O.		2.5	1	1.5	2	
		Paramag.	Dia	Para	Para	Para

imp.

$KO_2 + CO_2 \longrightarrow K_2CO_3 + O_2$

$NaO_2 + CO_2 \longrightarrow Na_2CO_3 + O_2$

used in Submarine & Space Crafts.

↑ This CO_2 released by respiration.

n.imp.

* Metal in liq. NH_3 :-

All alkali metals are soluble in liq. NH_3 ($-78°C$). These solutions have certain special properties.

1) They are paramag. at low conc. (3-4 molarity)
2) " " Blue colour " "
3) " " Bronz " High " (more than 4 mol-

4) On increasing the conc. ~~pra~~ paramagnetism that is magnetic susceptibility decreases.

5) These soln are good reducing agent, good conductors.

6) Conductivity decreases on increasing conc.

The above properties of metal NH_3 soln are due to presence of ammoniated cations and ammoniated electrons.

$$M \longrightarrow M^{\oplus} + e^-$$

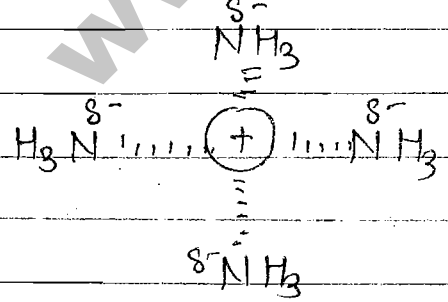
$$M^+ + x\,NH_3 \longrightarrow [M(NH_3)_x]^+$$
(l)

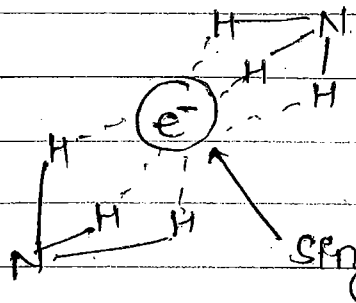
ammoniated or solvated cation.

$$e^- + y\,NH_3 \longrightarrow [e(NH_3)_y]^-$$

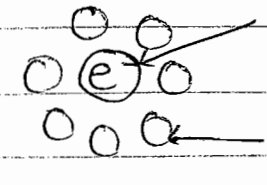
ammoniated or solvated electron.

$$M + (x+y)\,NH_3 \longrightarrow [M(NH_3)_x]^+ + [e^-(NH_3)_y]^{\ominus}$$





Single e^- responsible for paramagnatic character.



$\Rightarrow$ $Mam \rightleftharpoons M^{+}_{am} + e^{-}_{ammoniated}$ $K = 10^{+2}$ upto 3-4 molarity.

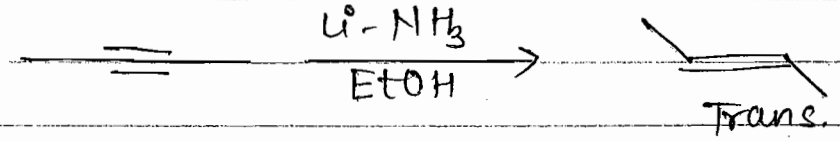
$M^{\ominus}_{am} \rightleftharpoons Mam + e^{-}_{am.}$ $K = 10^{-3}$ molarity > 4

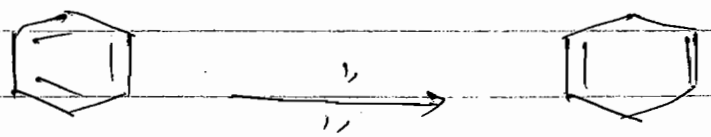
$2\,Mam \rightleftharpoons (Mam)_2$ $K = 10^{4}$

The properties of Metal ammonia sol^{n} are due to the of ammoniated e^{-}, but as the conc. increases. eqm. II favours & pairing of e^{-} takes place due to which magnetic susceptibility decreases. At higher conc eqm. III favours i.e dimer, trimers formed due to which colour fades i.e. Bronze.

Uses of M. NH_3 sol^{n}.

1) Strong reducing agent BIRCH Red^{n}.





High charge density on Metal
Suitable vacant orb.] to form complex.

imp ① $Fe(CO)_5 \xrightarrow[-30^\circ C]{Na - Liq.\ NH_3} Na_2[\overset{-2}{Fe}(CO)_4]$

② $Mn_2(CO)_9 \xrightarrow[\text{"}]{\text{"}} K[\overset{-1}{Mn}(CO)_4]$

imp ③ $K_2[Ni(CN)_4] \xrightarrow[\text{"}]{\text{"}} K_4[\overset{0}{Ni}(CN)_4]$

In these rxn. Metal in very low (-ve) oxidⁿ state

① Sodium penta carbonyl ferrate (-2) ← Negative O.S.

② Potassium tetra carbonyl Manganate (-1)

imp

COMPLEX formation Ability

Alkali metals have very less positive charge & bigger in size i.e. why they do not form complex easily.

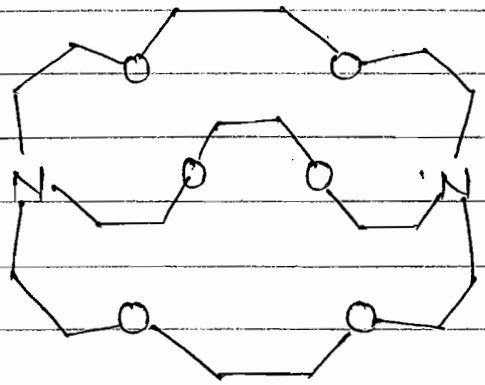
Ligand

- Normal lig.
  CO, CN^-, NO^+, H_2O, NH_3 etc.
- Special
  (Macrocyclic lig.)
  (Octopus Ligand)
  ↑
  Capture the metal
  Encapsulated lig.

$Na^{\ominus}$ ⇒ Sodide ion

Cryptand Ligand or Crypt.

↙Bicapped trigonal prismatic str.



Crypt-222
Octadentate

$$2Na + \text{Crypt-222} \xrightarrow[\text{or } NEt_2]{EtNH_2,\ -10^{\circ}C} [Na(\text{Crypt-222})]^{+}Na^{\ominus}$$

Stable even Na in −ve form.

* $[Na(\text{Crypt-222})]_2^{\oplus}\ C_{60}^{2-}$

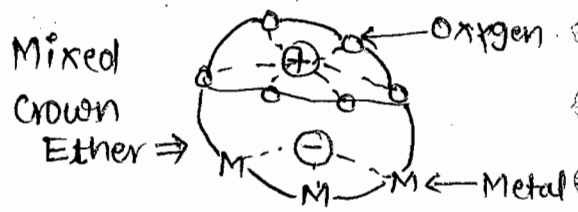
↑ Big cation ↑ Big anion.

Very stable complex.

Alkali metal have very low charge density & have poor tendency to form complex, but there are many special lig. which can form complex with them ex. Crypt, porphyrin ring, crown ether, macrocyclic tetra azide ring.

This crypt$^{\oplus}$ stabilise by $Na^{\ominus}$ ion.

कानो में मोतियाबिन्द ☺



Crypt - 211 with Li^+ ⇒ Stable complex.

Crypt - 221 " Na^+ ⇒ " "

Crypt - 222 " K^+ ⇒ " "

When Crypt - 222 Treated in acidic Medium then Amonium ($-\overset{+}{N}H_2$) forms.

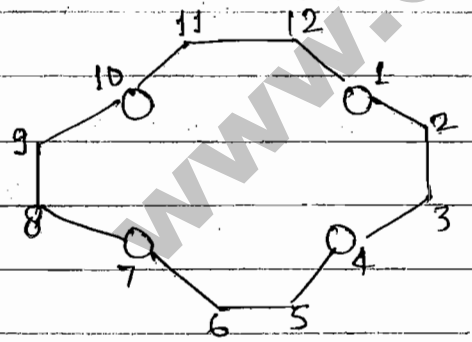
$\xrightarrow[\text{Medm.}]{\text{Acidic}}$

Both ~~ammoni~~ Nitrogen become $-\overset{\oplus}{N}H_2$

Now three isomers are possible.

* both H in
* both H out
* one in one out

Crown Ethers. O ⩾ 4



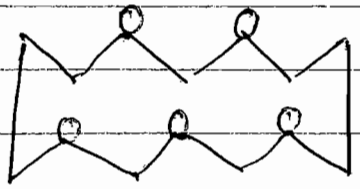
I.U.PAC. Name.

1,4,7,10 - Tetraoxacyclododecane.

4 - Crown - 12 General Name

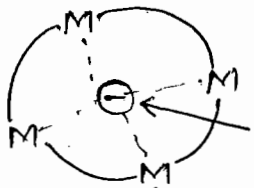
↑

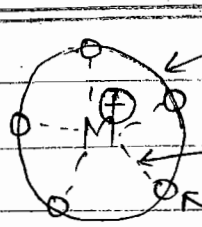
4 'O'

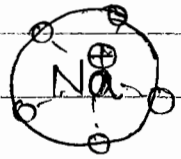


← Just like Crown.

Revise again and again.

Inverse Crown ⇒ 



* NaCl + Crown ether ⟶  + $Cl^{\ominus}$

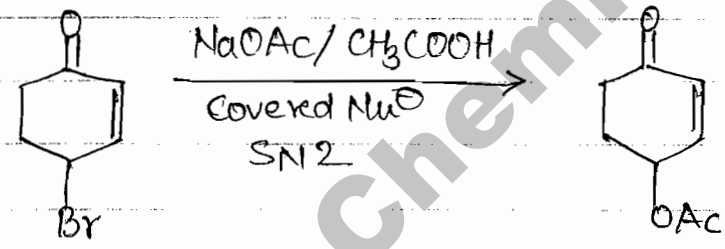
Free ion.

Crown ether increases the conc. of free $Cl^{\ominus}$

* NaCl + Benzene ⇒ Insoluble.

* NaCl + Benzene + Crown ether ⇒ Soluble

* Crown ether used as phase transfer catalyst.

Imp. 

Nacked $Nu^{\ominus}$ E_2 | NaOAc/Crown ether ⟶ 

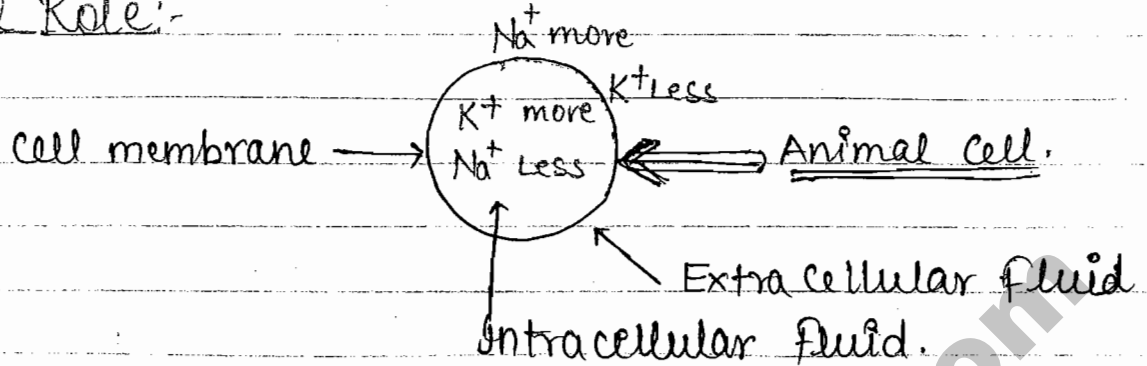
↑ Increasing the conc. of $OAc^{\ominus}$ (Negative ion)

⇒	4 - Crown - 12	Li^+	Particular ion forms complex with special Crown ether.
	5 - Crown - 15	Na^+	
	6 - Crown - 18	K^+	
	7 - Crown - 21	Rb^+	
	8 - Crown - 24	Cs^+	

Banana rich source of K^+ ion.

Na^+/K^+ Pump

Biological Role:-



$1ATP \longrightarrow 1ADP + ip + E$

↑ inorganic phasphate

+ve charge on outer side of memb.

→ + + + + + + ← cell membrane.

− − − − − −

↑

−ve charge on inner side of memb.

*Since both charges are opposite ⇒ Potential Gradient

⇓

Responsible for Nerve Impulse (Sence).

Valinomycin ⇒ just like Crapt.

COMPOUNDs :-

Solubility :- The solubility of ionic comp. depends upon two factors mainly - Lattice energy, & Hydration energy.

* Both HE & LE depends upon std. size of anion & cation. but L E depends more on size of anion becoz anion are fnt at lattice point becoz they are str. governing.

* In case of s-block - the solubility generally decreases on top to bottom however this trend may be change, when -
i) if anion show high hydration eg. F^-, $\bar{O}H$
ii) Large size of anions. CO_3^{--}, oxalate, bicarbonate-

⇒ In general

1 Group

Generally
Sol. ↓
But for
F^-, $\bar{O}H$, CO_3^{--}
$\bar{O}X^-$, HCO_3^-
Solubility ↑

2 Group

Generally solubility ↓
But for $F^{\ominus}$, $\bar{O}H$,
$C_2H_4^{--}$
Solubility ↑

Li^+ & Be^{2+} very small i.e. why they have very high heat of hydration. Li^+ salts are usually having water of crystalisation i.e. hydrated. & generally they are tri hydrated.

29/09/2014

* $Li^+Cl^- + aq. \xrightarrow{\text{Crystalisation}} Li^+Cl^- \cdot 3H_2O$

Hygroscopic ⇒ Absorbe H_2O & don't form sol^n, Ex. $CaCl_2$
Deliquiscent ⇒ " " " form sol^n. Ex. NaOH
Efflourescent ⇒ Releases H_2O Ex. $CuSO_4 \cdot 5H_2O$

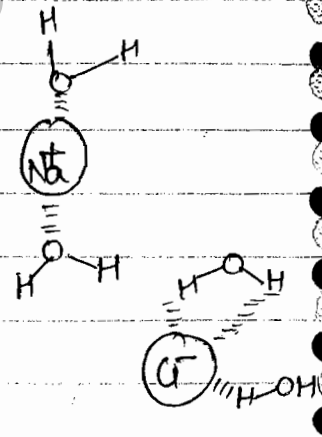
HYDRATION & CONDUCTANCE :-

$Na^+ \cdots Cl^- \xrightarrow{aq} Na^+ + Cl^-$

↑ Eletrostatic attraction.

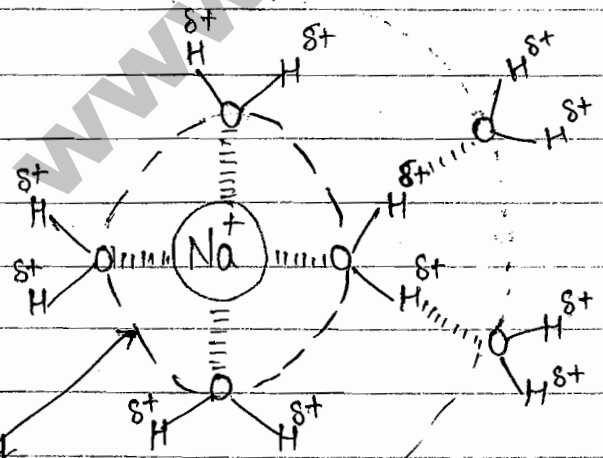
$Na^+ \downarrow H_2O$ $\quad Cl^- \downarrow H_2O$

$[Na(H_2O)_x]^+ \quad [Cl(H_2O)_y]^-$



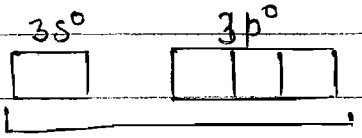
When one mole of ionic solid is dissolve in water, the energy ~~red~~ released is called hydration Energy.

Hydration No. The average no. of H_2O molecule attracted by central metal ion.



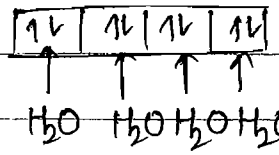
Group के First & last element ही generally Abnormal behaviour show करते हैं।

$Na^{\oplus}$ = $1s^2, 2s^2, 2p^6, 3s^0, 3p^0$

$Na^{\oplus}$ 

sp^3 hyb.

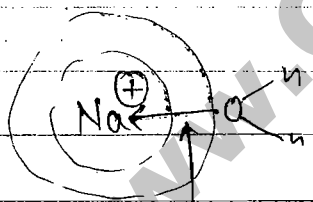
sp^3 hyb. of $Na^{\oplus}$ in aq. soln.
'Td' Geometry.

$(Na^{\oplus}4H_2O)$. 

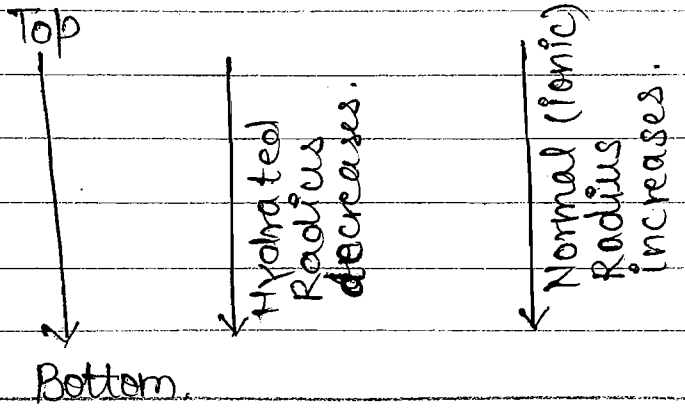
Hydration no. depends upon charge density as well as available space around central metal ion.

H. No. or Co-ordination No.

$Li^{\oplus}$	4 rarely 6
$Na^{\oplus}$	4
$K^{\oplus}$	4, 6
$Rb^{\oplus}$	4, 6
$Cs^{\oplus}$	no



Almost Covalent bond.
because very strong.



जिस cell पर Oxidn. हो ⟹ Anode
" " " Redn. " ⟹ cathode

SO_4^{--} NO_3^- OH^- X^- स्नॉमस

Tendency of Oxidn. ↑

↓

S NOx

Imp.

Conductivity of $Li^{\oplus}$ in aq. soln. less than Cs becoz $Li^{\oplus}$ surrounded by H_2O mol. hence less conductivity. while $Cs^{\oplus}$ does not interact H_2O due to bigger size so it is free to move ⟹ conductivity more.

* Hydration Energy of II group is more than I group becoz charge is more in II group. Ex. $Na^{\oplus}$, Mg^{II}

Electrolysis of Salt--

Anode (Oxidn.)

$2Cl^- \xrightarrow{Oxdn.} Cl_2 + 2e^-$

$\bar{O}H \longrightarrow X$

cathode (Redn.)

$Na^+ + e^- \longrightarrow X$

$2H^{\oplus} + e^- \longrightarrow H_2$

$\rightarrow NaOH$

E.C.S. में नीचे है तभी आसानी से e^- ले लेगा

* Alkali metals can't be prepared by their aq. salt soln.

"Dawn" discovered a new method for electrolysis. he electrolyse molten solution using inert electrode.

$NaCl \longrightarrow Na^{\oplus} + Cl^{\ominus}$

molten

Anode

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

cathode

$$2Na^{\oplus} + 2e^- \longrightarrow 2Na$$

Here is no competition of $\ominus$ in oxidⁿ. b/ω Cl^- & $\bar{O}H$ so Cl^- easily oxidised & also not competition b/ω $Na^{\oplus}$ & $H^{\oplus}$ so $Na^{\oplus}$ easily reduced on cathode.

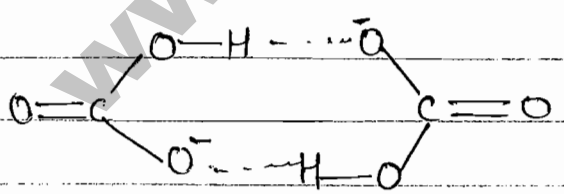
Carbonates & Bicarbonates

The solid bicarbonates are ~~f/a~~ known only for alkali metal.

⇒ Only $LiHCO_3$ (Li bicarbonate) exist in solⁿ. phase other exist in solid phase.

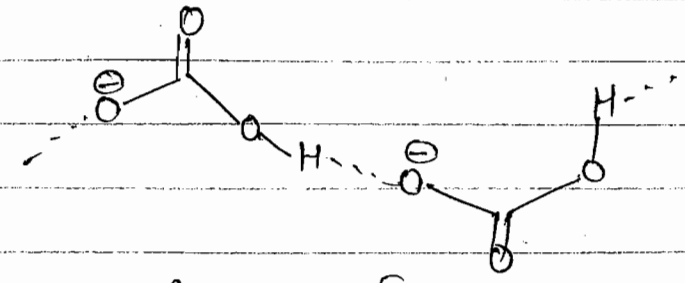
⇒ II group bicarbonate exist in solⁿ. phase.

⇒ In solid state alkali metal bicarbonate ⊕ specially of Sodium & Potassium show Hydrogen bonding.



Cyclic dimer

Bicarbonate of $Na^{\oplus}$



Zig. zag form.

Bicarbonate of $K^{\oplus}$

$PbI + ZnS + BaSO_4$ ⇒ चूहा मार दवा

Inscisor teeth of Rat grow up life time i.e. why they use their teeth more & more.

Sulphates :- Solubility top to bottom decreases.

$BaSO_4$ (Poision) ⇒ Highly insoluble
Rat Killer

Due to less solubility it can't effect when taken externally, but effect when taken internally (means when injected)
Ultrasound के time $BaSO_4$ पिलाया जाता है।

* Be, Mg colourless in Bunsen Burner flame
⇓
Less energetic
⇓
Less excitation of e^- of Be, Mg ⇒ No colour.

Carbide :- ~~Carbon~~ Comp. in which carbon is more electronegative than metal.

Be_2C] covalent

CaC_2
Mg_2C_3 } ionic
Al_4C_3

$$Be\overset{2OH^- \; -2H^+}{=}C\overset{2H^- \; -2OH}{=}Be \xrightarrow{4H_2O} 2Be(OH)_2 + CH_4$$

H_2O → CaC_2 ← As you provide H_2O in CaC_2 it provide acetylene gas. which create press. in pot.

* $Al_4C_3 \longrightarrow 4Al^{3+} + 3C^{4-} \xrightarrow{12H_2O} 4Al(OH)_3 + 3CH_4$

* $CaC_2 \xrightarrow{H_2O} Ca(OH)_2 + HC\equiv CH$ — Used in Belding

$CaC_2 \downarrow$

$Ca^{2+} + \overset{\ominus}{C}\equiv\overset{\ominus}{C}$

$2H^{\ominus} \text{---} 2H^{\oplus}$

* $Mg_2C_3 \equiv 2Mg^{++} + C_3^{----}$

$\Downarrow$

$\bar{C}\equiv C-\bar{C}-\bar{C}-$

$\xrightarrow[H_2O]{} Mg(OH)_2 + HC\equiv C-CH_3$ Propylene

* $Ca + 2C \xrightarrow[\text{electric furnish}]{1100^\circ C} CaC_2 \xrightarrow[N_2]{>1100^\circ C} \underline{CaNCN} + C$ — Fertilizer

$CaCN_2$

calcium Cynamide

Ca^{2+} $\bar{N}=C=N^-$

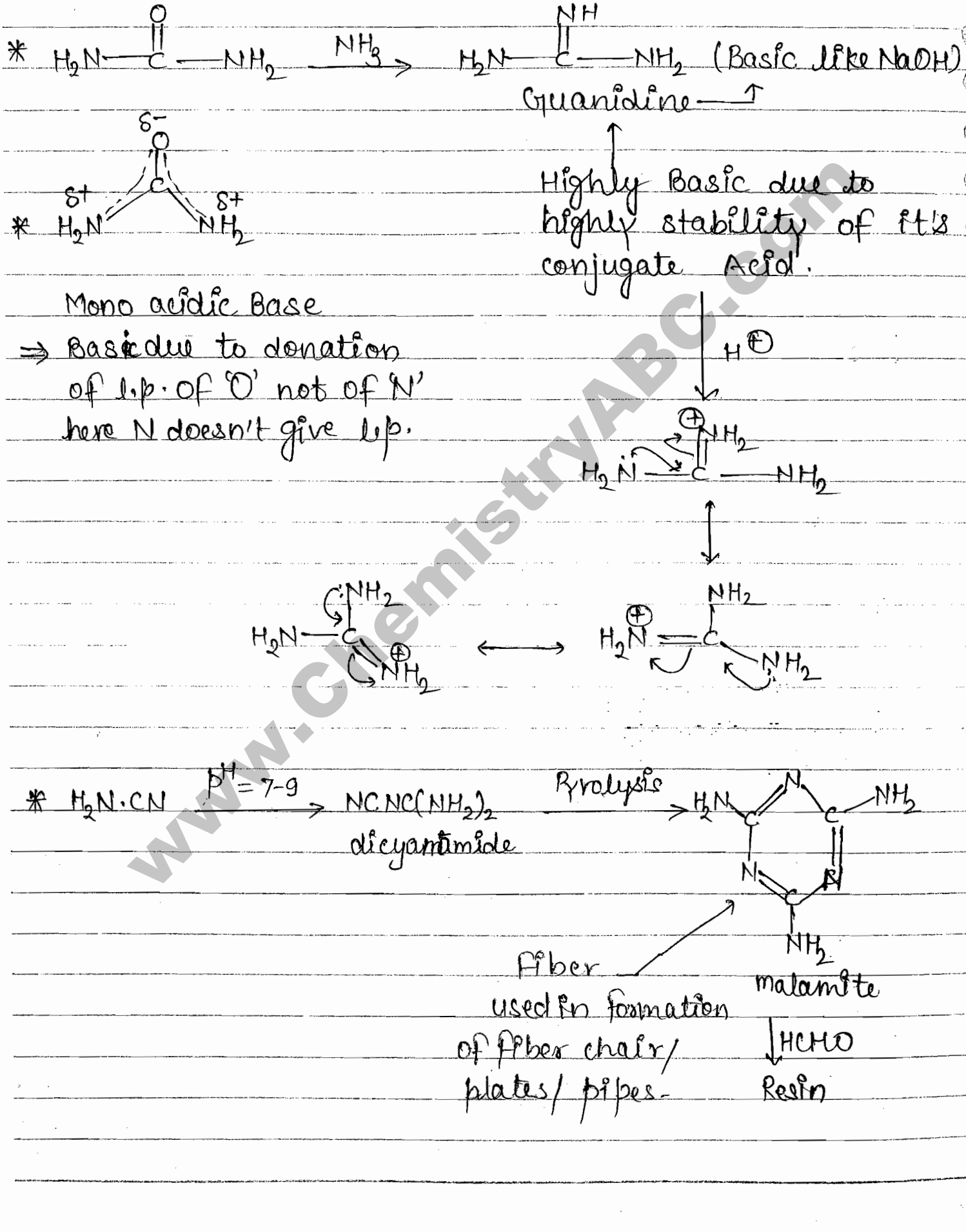
$CaCN_2$

* $CaNCN + H_2SO_4 \longrightarrow CaSO_4 + H_2NCN$ Caynamide

$H_2N-C\equiv N$

H_2O ← $H_2N-\overset{O}{\overset{\|}{C}}-NH_2$ Urea

H_2S → $H_2N-\overset{S}{\overset{\|}{C}}-NH_2$ thio urea.



Bond dissociation Energy of CO & N≡N is highest in all the diatomic molecules.

Nitrides

$M + N_2 \longrightarrow$ No Rxn.

M = Alkali metal

Only $Li + N_2 \longrightarrow Li_3N$

Ist group.

* Li reacted with N_2 because it's is Lattice energy is more which is sufficient to break N≡N bond.

* Mg & Ca are Sweeper element (or) Scavenger of N_2 because wherever they found N_2 they react easily

$Mg + N_2 \longrightarrow Mg_3N_2$

$Ca + N_2 \longrightarrow Ca_3N_2$ Mg, Ca सफाई कर्मी

Nitrate

T.S.↑

Na_3N	Mg_3N_2	
T.S.↓	↓	T.S.↓
K_3N	Ca_3N_2	

T.S.↓

Na_2CO_3	$MgCO_3$	
T.S.↑	↓	T.S.↑
K_2CO_3	$CaCO_3$	

Nitrate

T.S. ↓

$NaNO_3$	$Mg(NO_3)_2$
KNO_3	$Ca(NO_3)_2$

T.S. ↑ (down the left column)

T.S. ↑ (down the right column)

* $MNO_3 \xrightarrow{\geq 500^\circ C} MNO_2 + O_2$

MNO_3: Alkali metal Nitrate

MNO_2: Nirite

* Exception.

$LiNO_3 \xrightarrow{\Delta} [LiNO_2] + O_2$

$[LiNO_2] \rightarrow Li_2O + N_2$

$O_2 + N_2 \rightarrow NO_2$

Hydride

I group.		II group.	
Top.	Reactivity towards H_2 ↓	Top.	$(BeH_2)_n$, $(MgH_2)_n$ — Polymer.
Bottom.		bottom.	

⇒ $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$

Hydrolith

Industrial method to prepare H_2 gas ↑

* Alkali hydrides are highly Basic they provides $H^{\ominus}$ ion.

* $HC\equiv CH + NaOH \longrightarrow$ No Rxn.

$HC\equiv CH \xrightarrow{Na} HC\equiv C^{\ominus}Na^{\oplus} + \frac{1}{2}H_2$

$HC\equiv CH \xrightarrow{NaH} HC\equiv C^{\ominus}Na^{\oplus} + H_2$

All the metals atoms more basic than their hydroxides.

$NaH > Na > NaOH$

↑

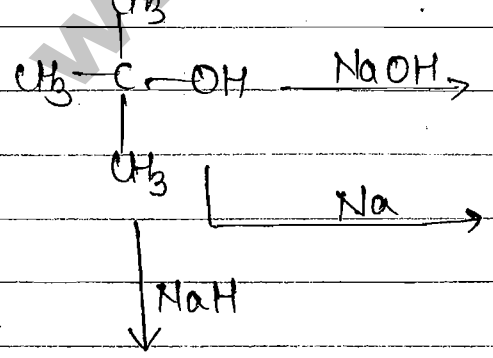
Hydrides are more basic than their corresponding metal

* $CH_3-CH_2-CH_2-OH \xrightarrow{NaOH}$ Almost no Rxn.

$CH_3-CH_2-CH_2-OH \xrightarrow{Na} CH_3CH_2-CH_2-O^{\ominus}Na^{\oplus} + \frac{1}{2}H_2\uparrow$

$CH_3-CH_2-CH_2-OH \xrightarrow{NaH} CH_3CH_2CH_2O^{\ominus}Na^{\oplus} + H_2\uparrow$

*



KOH is more polar than NaOH. & also more basic

Soft Soap ⇒ made by Pot. (K) ⇒ Bathing soap.

Hard " ⇒ made by Na ⇒ Washing soap.

~~Powder Soap ⇒ Zn salt.~~

NaOH कास्टिक सोडा

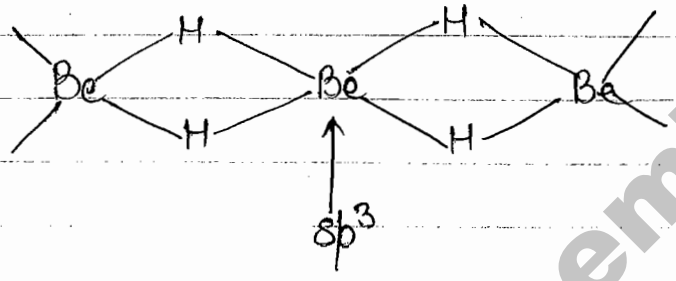
⇒ Enamel ⇒ $Ca_5(PO_4)_3OH \rightleftharpoons 5Ca^{++} + 3PO_4^{3-} + \overset{\ominus}{O}H$

Hydroxy apatite

Mg ⇒ Chlorophyl.

M. Imp

Polymeric & Organometallic Compound:-



Be = $1s^2$ $2s^2$ $2p^3$

G.S. ↑↓ — — —

E.S. 1 1 — —

sp^3 hyb.

3-Centered - 2 - electron bond.

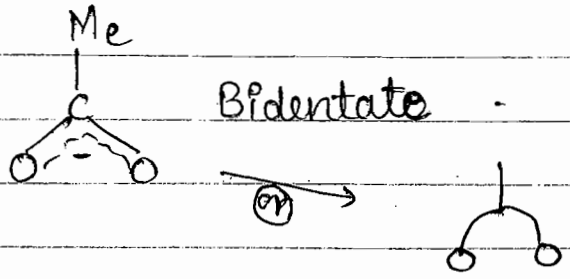
(or)

Banana (or) Father bond

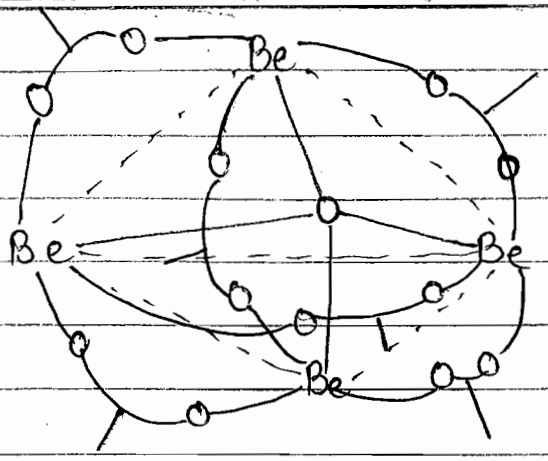
Imp.

* $[Be_4O(CH_3COO)_6]$ Basic beryllium acetate

$[Be_4O(NO_3)_6]$ " " Nitrate Both used in making Pearl.



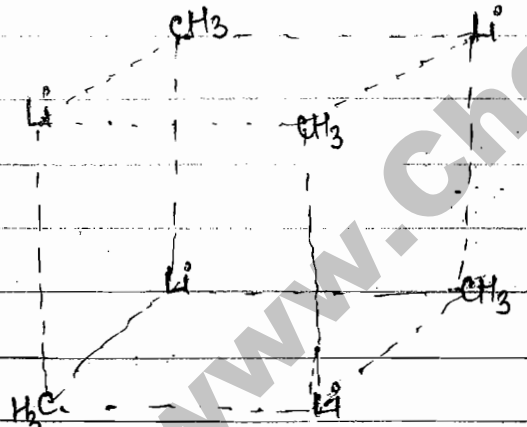
Cube contains two Tetrahedral so splitting will be double magnitude & cube is centrosymmetric so gerade will be written. i.e. e_g & t_{2g}



Alkyl lithium

$(CH_3Li)_4$

Methyl lithium exist in tetrameric form in cubic lattice. Lattice 8 particles placed at 8 cornor of cube.



unit cell of $(CH_3Li)_4$

Both Li & CH_3 exist in 7 co ordination no.

C = 3H + 3Li + 1Li = 7

Li = 3C + 3Li + 1C = 7

Most Imp

p- Block Chemistry

BORON Family

Triel Group

⇓

These groups shows 3 valency

B ← Non metal.

Al, Ga, In, Tl] Metal.

Atomic Size:

B < Ga < Al < In < Tl

Zeff. Ga > Zeff Al.

↓

Because it has f orb. ⇒ less shielding.

Ionisation Energy:-

B > Al < Ga > In < Tl

↑ Due to Zeff. more I.E.

↑ due to lantheride contraction more I.E.

Melting Point & Structure:-

Melting point of this group element shows irregular pattern. It firstly decreases upto Ga then increases upto Tl. B has the highest m.p. in the gp. The abnormal m.p. due to diff. crystal str. 'B' exists in B_{12} icosahedral str. with 12 corners and 20 triangular faces. 5 allotropic forms are k/n. in which α & β are common all posses B_{12} str. in which each B having 5 nearest neighbour at 5.18 Å.

m.p.

Ga, Hg, Cs are liq. at R.T.

30/09/2014

Imp.

B m.p. >2000°C (Highest)

Ga m.p. 25°C Lowest

B_{12} dodeca atomic

C_{11} Hemidec (or) Undec

C_{20} icos

C_{30} tricot

C_{40} Tetracot

C_{100} Hect

C_{1000} - Kilia

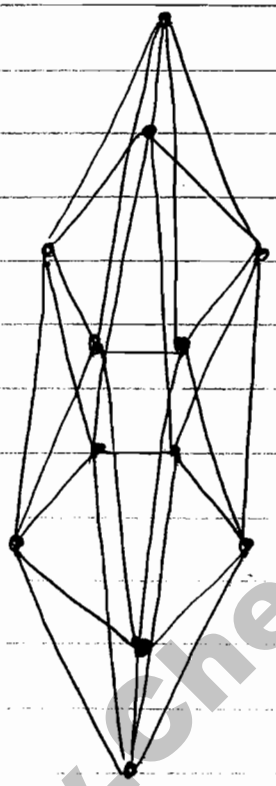
C_{2000} dilia

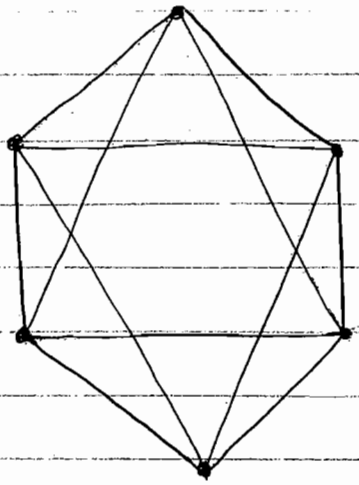
Deltahedron.

Δ + Hedron

↓

face





Icosahedra Str.

2C - 2e⁻ bonding

3C 2e⁻ bonding

Simple Str.

In B_{12} there 2C-2e⁻ & 3C 2e⁻ bonding i.e. multi-centred bonding. On the basis of ionisation energy, B

Lamp black (देहात का दिया) ⇒ having Fullerene.

HCP
↑

should be more metallic than Gold. but Gold is metallic while B is non metal because in Au the no. of nearest atom are 12 while in B is 5.
More the nearest atom ⇒ more will be metallic character.

'Ga' has only one nearest neighbour i.e. it exist in diatomic form i.e. why it's m.p. is lowest in group. Ga has special feature in density, the density of solid Ga is less than liq. Ga. due to with which solid Ga float on liq. Ga, This behaviour is also shown by Bi, Ge, H_2O.

Nature of Bonding :-

$$B \xrightarrow[I_1 + I_2 + I_3]{-3e} B^{3+}$$

↑ Boron never forms B^{3+} becoz it's I.E. ($I_1 + I_2 + I_3$) are very high due to it's small size. i.e. why Boron never form ionic comp.

AlF_3 ionic

$AlCl_3$
$AlBr_3$
AlI_3
} covalent

Al^{3+} ... Cl^-
Big size
more polarisation.
so covalent.

A^{3+} ... F^-
Small size
less polarization,
so ionic.

Ge, Ga, Bi, H_2O ⇒ solid form has less density than liq. form.

$AlCl_3$ ⇒ Solid but highly ~~stable~~ soluble in H_2O

$\downarrow \Delta$

$Al^{3+} + 3Cl^-$ $\quad \Delta H = +5137$

$Al^{3+} + H_2O \longrightarrow [Al(H_2O)_6]^{3+}$ $\quad \Delta H = -4665 \times 1$

$3Cl^- + H_2O \longrightarrow 3[Cl(H_2O)_4]^-$ $\quad \Delta H = -381 \times 3$

$\Delta H = -5808$

↑ More Hydration Energy then Energy of decomposition.

Almost

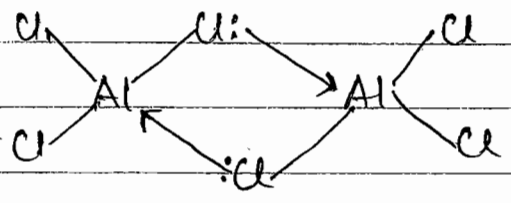
* All the Al^{3+} comp have 6 co ordination no.

* Top to bottom ~~hydr~~ solubility decreases.

* $AlCl_3$ ⇒ Highly Hygroscopic.

* $AlCl_3$ $\quad > 800°C$ monomeric form.
$\quad < 400°C$ dimeric form

Imp.



2 - Co-ordinate bond.
6 - Covalent bond.

Where B or Si comp +nt guess for π bonding.

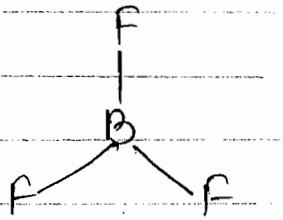
$AlCl_3$ | Lewis acidity
$AlBr_3$ | character ↓
AlI_3 ↓

Al →→ Cl ← More electroneg.

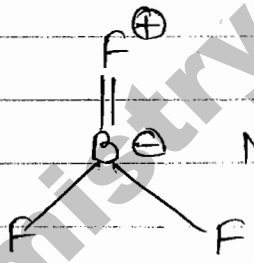
Al ⟶ I Less electroneg.

* BF_3 ← (more) Back donation (Least lewis Acid)
BCl_3
BBr_3 | Top to bottom lewis acidity ↑
BI_3 ↓ Top to bottom B.O. ↓ i.e. bond strength ↓
i.e. stability decreases.

*



(Less stable)



More stable (B octet complete)

* In $AlCl_3$ π bonding almost negligible due to 3p - 3p π bonding.

* Halides of 'B' exist in monomeric form becoz. 'B' is very small so on dimerisation steric crowding increases. Back π-bonding is also have major role to retain in monomeric form.

* 'Al' halides. dimerises, size of Al big, no π-bonding.

$NH_3 \xrightarrow{H_2O} \overset{\oplus}{N}H_4\overset{\ominus}{O}H$ ✗

This comp. doesn't exist in world.

$NH_3 \cdot H_2O$ ← It's only dilute soln of NH_3

---

* Adduct formation depends on Nature of ligand, solvent, HSAB concept.

Q F—B bond stretching freq? in these adducts.

$BF_3 \leftarrow OR_2$ ①

More B.O. of B—F

Highest $h\nu_{B-F}$

$BF_3 \leftarrow NH_3$ ②

$BF_3 \leftarrow NEt_3$ ③

Least B.O. of B—F

⇓

Least $h\nu_{B-F}$

$h\nu_{B-F}$ ③ < ② < ①

⇒ Thermal Stability order ① > ② > ③ ← Less B.O. Less T.S.

↑ More B.O., more T.S. of B—F

Every Yr. M.Imp

BORIC ACID

$B(OH)_3$ Right

H_3BO_3 Wrong

⇒ Borax (सुहागा) ⇒ Tincal

↓

$Na_2B_4O_7 \xrightarrow{H_2SO_4(aq)} B(OH)_3 + Na_2SO_4$

Effect of Heat.

$B(OH)_3 \xrightarrow[100^\circ C]{\Delta} HBO_2$

$-H_2O$

$(HO-B=O)$

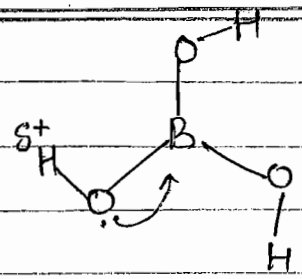
$4HOB{=}O \xrightarrow[160^\circ C,\ -H_2O]{\Delta} H_2B_4O_7 \xrightarrow[\Delta]{\text{Red hot}} B_2O_3 + H_2O$

Meta boric acid

Boric anhydride
(or)
Boron oxide

Acid.	Anhydride / oxides.
$\overset{+3}{B}(OH)_3$	B_2O_3
$H\overset{+3}{N}O_2$	N_2O_3
$H\overset{+5}{N}O_3$	N_2O_5
$H_2\overset{+6}{S}O_4$	S_2O_6
$H\overset{+7}{C}lO_4$	Cl_2O_7
$H\overset{+7}{C}lO_4$	Cl_2O_7
$H\overset{+5}{C}lO_3$	Cl_2O_5
$H_3\overset{+5}{P}O_4$	P_2O_5
$H_3\overset{+3}{P}O_3$	P_2O_3 ← Oxidn state of 'P' in H_3PO_3

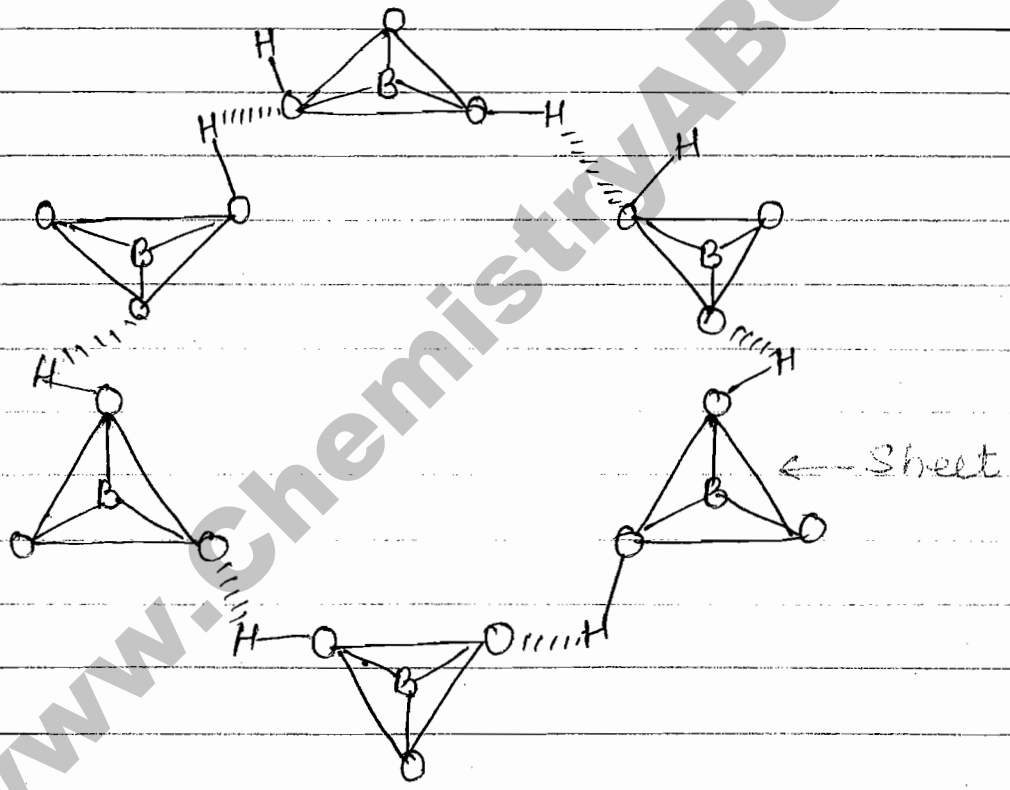
↑ Oxidn state of oxygen.



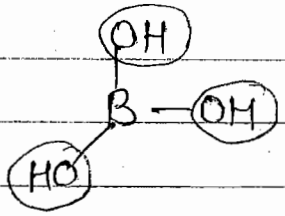
$\mu \neq 0$

π-bonding present. 2p. - 2p. bonding.

Boric acid shows Hydrogen Bonding & forms planar sheets.



Q How many H.B. in $B(OH)_3$



6 Atoms (3'O' + 3'H') responsible for H.B. so H.B. = 6.

B A ≠ A A

All Bronsted acid are arhenius acid. & vice versa.

B B ≠ A B

All Bronsted Base are not arhenius base.

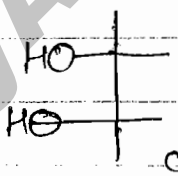
* $B(OH)_3 + \overset{\oplus}{Na}\overset{\ominus}{O}H \rightleftharpoons Na[B(OH)_4]$

(or)

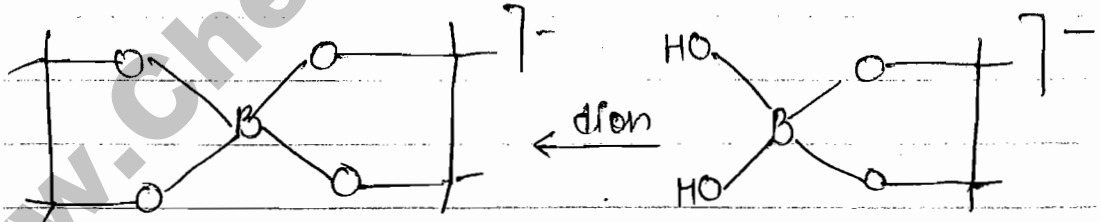
$NaBO_2 \cdot 2H_2O$

Sod. metaborate

* $B(OH)_3 + \bar{O}H \rightleftharpoons B(OH)_4^-$ + cis-diol



$\xrightarrow{-H_2O}$



Boric acid, due to its weak acidic nature show incomplete titration. i.e. end point can't be determine easily therefore to move the rxn in forword direction to get the sharp end point cis diols like glycerol, ethylene glycol etc are used also Glucose, Sucrose -- can be used.

M. Imp NET

Cis - diol used.

Borates:- Metallic salts of Boric acid.

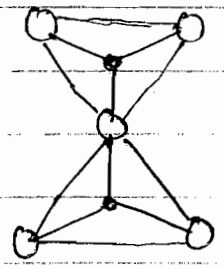
BO_3^{---}

* Ortho Borates B - sp^2
  ↳ free state or discrete form.

  BO_3^{---} unit

  eg. $AlBO_3$, $Mg_3(BO_3)_2$

* Pyro borates B - sp^2
  one 'O' is shared b/w two units



(or) $B_2O_5^{4\ominus}$

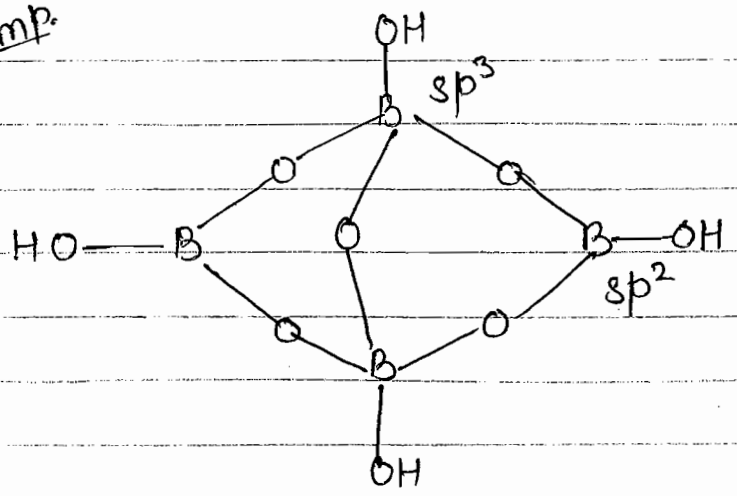
* Meta Borates :- Having BO_2 units. B - sp^2
  Two 'O' are generally shared.

i) Cyclic Borates $Na_3B_3O_6 \Rightarrow NaBO_2$

ii) Linear Borates $[Ca(BO_2)_2]_n$

* Mixed Borates :- Two kind of B' sp^2 B & sp^3 B.
  Eg. Borax.
  NET 2010
  $Na_2B_4O_7 \cdot 10H_2O$

Imp.



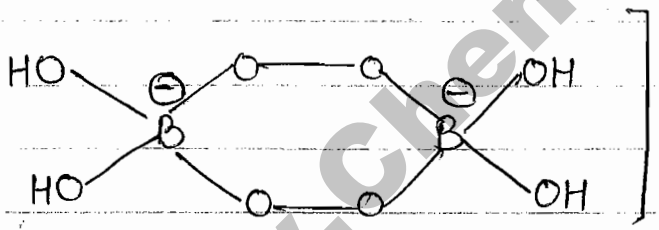
$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

Actual formula of Borax.

* Peroxoborates :-

↑ पर लगे हैं ⇒ peroxide bond.

$[B_2(O_2)_2(OH)_4]^{--}$



चार बूँदों वाला उजाला

optical Whitener ⇒ Used in Ujala (नील)

Imp.

AL.UMS ⇒ Double salts

General formula :- ↓

Eg. [illegible] · $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Imp

$[\overset{I}{M}(H_2O)_6]^{+}\,[\overset{III}{M}(H_2O)_6]^{3+}(SO_4)_2 \cdot 12H_2O$

Univalent metal ⇒ [illegible], Tl^+, Ag^+, Au^+, K^+

Trivalent metal. Cr^{3+}, Fe^{3+}, Co^{3+}, Al^{3+}

H_2SO_4 Oil of Green vitriol

01/10/2014

All Alums are isomorphic (same str & formulae).
↑ such comp can't be separate by normal crystallization.

$ZnSO_4 \cdot 7H_2O$ White vitriol.

$FeSO_4 \cdot 7H_2O$ Green vitriol.

$MgSO_4 \cdot 7H_2O$ Magnecium vitriol.

* $\overset{II}{M}SO_4 \cdot \overset{III}{M_2}(SO_4)_3 \cdot 24H_2O$ Pseudo Alum.

↑
Mg^{2+}, Ca^{2+}
Zn^{2+}, Cu^{2+}

* Li^+ does not form Alum or Pseudo Alum.

Borax Bead Test:

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-5H_2O]{100^\circ C} Na_2B_4O_7 \cdot 5H_2O \xrightarrow{160^\circ} \downarrow -5H_2O$$

Sod. meta Borate
↓
Boric anhydride → $B_2O_3 + 2NaBO_2$ ← $Na_2B_4O_7$ (Δ)

Bead ← मीठे नाले बनाशा की तरह

Blue ← $CuSO_4$
Colour

$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$

$B_2O_3 + CuO \longrightarrow$ Metaborates (Blue)
$NaBO_2$

Vitamin ⇒ वाइटामन ✓

Vitamine ⇒ विटामिन X

Cu → Blue colour with Bead ($B_2O_3 + NaBO_2$)

Cr → Green " " "

Co → Blue " " "

This was the first experiment by which presence of Co has been stabilised in Vit-B_{12}

imp

BORANES

B_2H_6 $2x - 6 = 0$, $x = +3$ O.S. of B.

Boranes are the binary comp of the Boron & Hydrogen.

$B_2H_6 \xrightarrow[\text{Methylation}]{Me_2SO_4} B_2H_2Me_4$

↓

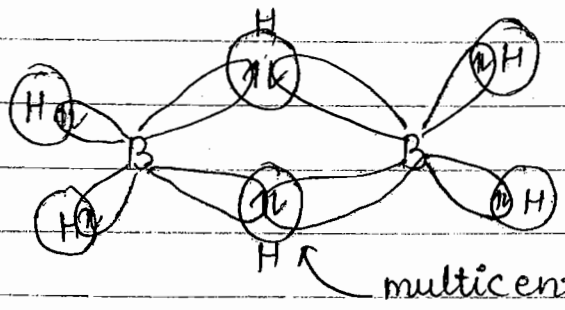
2 signals in ^1H-NMR

B(5) = $1s^2\ 2s^2\ 2p^1$

G.S. $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ ___

E.S. $\uparrow$ $\uparrow$ $\uparrow$ ___

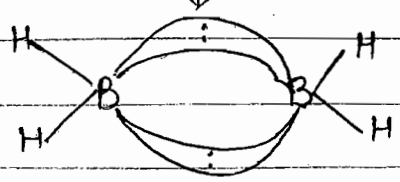
sp^3 hyb.



$Ph-CH_2-OH \xrightarrow{MnO_2} Ph-\overset{O}{\overset{\|}{C}}-H$ only oxidised upto ald.

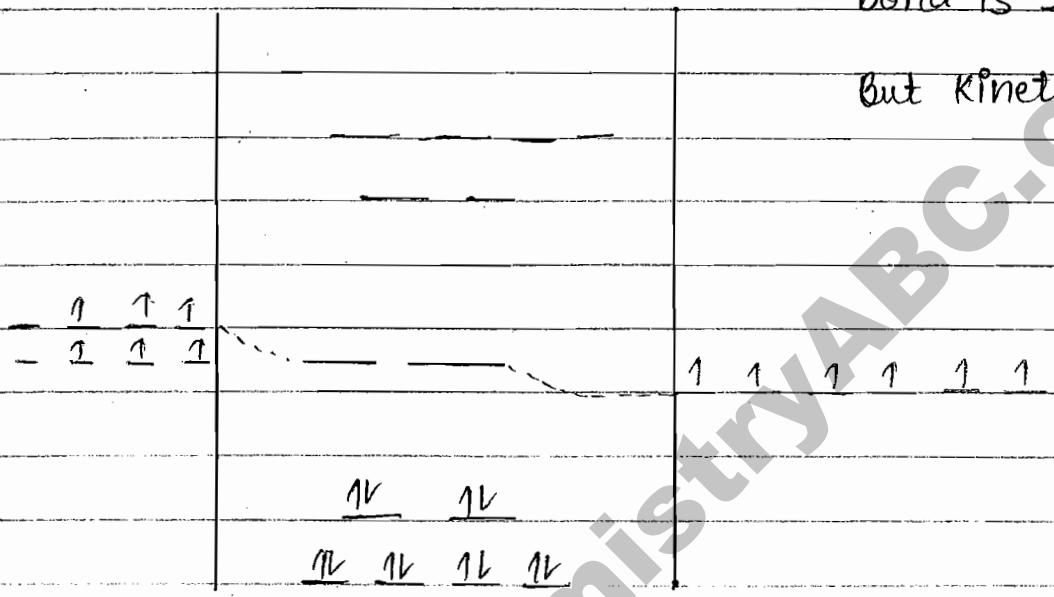
$R-CH_2-OH \xrightarrow{MnO_2} R-COOH$ oxidised upto acid.

Father / Banana Bond.



⇐ 6 Bonds in B_2H_6

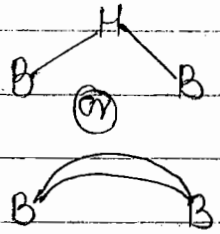
↑ ½ Bond order in banana bond so bridged bond is weak. (Thermally less stable)
But Kinetically more stable



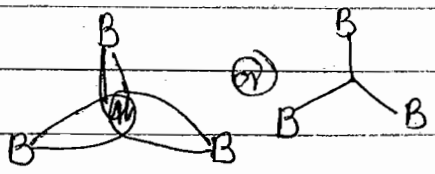
Since bridged bonds are kinetically more stable (becoz there is more overlapping so requires more Ea to break bridge bonding) so Me_2SO_4 can't break bridged band but breaks terminal bond.

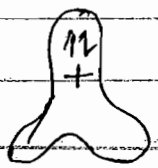
Multicentre Bonding

3C, 2e⁻ Banana Bonding



3c, 2e⁻ closo bond





* All boranes are Lewis acid becoz their Non bonding orbital is vacant.

Type of BORANES

Super-Super Closo, Super closo, Hyper closo, closo, Nido,
$B_nH_n^{++++}$ $B_nH_n^{++}$ B_nH_n $B_nH_n^{2-}$ $B_nH_n^{4-}$

Arachno, Hypo, Klado
$B_nH_n^{6-}$ $B_nH_n^{8-}$ $B_nH_n^{10-}$

CLOSO Borane ⇒ Parent Borane.

~~CLO~~ No Neutral closo borane exist they exist in ionic form. Ex. B_4H_6 not exist. (Neutral)

$B_4H_4^{2-}$ exists. (ionic form)

* B_4H_6 Tetrahedral
  B_6H_8 Octahedral.
  $B_{12}H_{14}$ Icosahedral

} All are CLOSO.

Conjucto Boranes:-

Those boranes which exists in more than one str. unit.

Acid ↑ M.gmP

ARACHNO Boranes are more acidic than Nido & also more stable.

* Ionic closo are highly stable due to 3 dimentional aromaticity.

⇓

Non planar but aromaticity exist

Nido B_nH_{n+4} Eg. B_4H_8, B_5H_9, B_6H_{10}

ARACHNO B_nH_{n+6}

B_4H_{10}, B_5H_{11}, B_6H_{12}

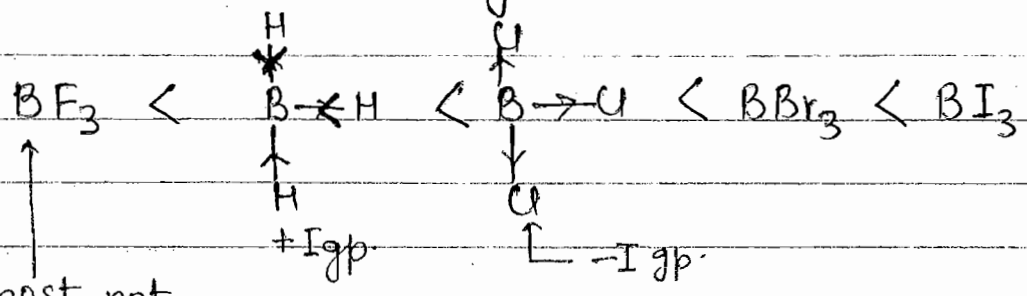
* As the decapping increases then, acidity also increases.
* if Same type Str. of ~~Acid~~ Borane then More the no. of Boron atoms, more will be lewis acidity because more no. of B atoms more will be Non bonding orb ⇒ Responsible for Lewis acidity.

for eg. Nido series.

$B_4H_8 < B_5H_9 < B_6H_{10}$

acidity ↑

* Lewis Acidic strength.



Isolobality:- e⁻ count & str. should be same then isolobal. (Vertices should be same).

Q. which is a isolobal. $\overset{\ominus}{C}H_3$, $\ddot{N}H_3$, H_2O, PH_3, CH_4

These are iso electronic & having 3 Vertices ⇒ Isolobal.

Isoelectronic

C — 4 — BH ⇒ $B^{\ominus}$ — 4

N — 5 — BH_2 ⇒ $BH^{\ominus}$ — 5

* $B_{10}H_{14} + 2R_2S \longrightarrow B_{10}H_{12}(R_2S)_2 + H_2$

Nido

↓ $R-C\equiv C-R$ or R_2S_2

$R_2C_2B_{10}H_{10} + 2R_2S + H_2$

(or)

$C_2B_{10}H_{12}$

$R_2C_2B_{10}H_{10}$ if R = H

$B_{12}H_{14}$ CLOSO

$H_2C_2H_{10}H_{10}$ → ortho because carbon comes from acetylene

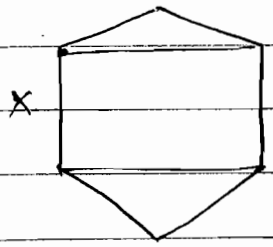
(or)

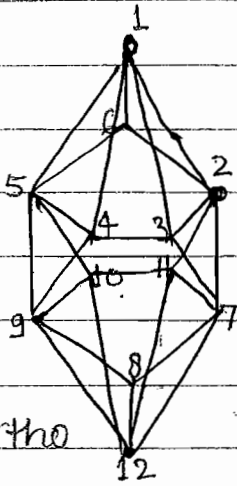
Icosahedral

$C_2B_{10}H_{12}$ First Carborane which can't approach via meta or para position

CLOSO

$C_2B_{10}H_{12}$





1,2 ortho (If carbon on 1 & 2 position)

1,7 - meta

1,12 - para

Stability para > meta > ortho

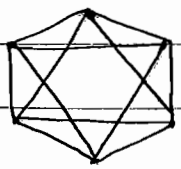
Q for ortho $C_2B_{10}H_{12}$ most acidic 'B' are ?

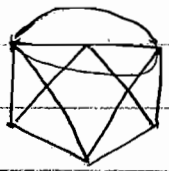
Carbon is more electronegative than 'C' so 'B' attached with 'C' is more acidic.

B (position 2 & 3) directly attached with both 'C' atoms so most acidic. C (position 12) is least acidic more distance from 'C' atoms.

$B_{12}H_{12}^{2-}$ or $C_2B_{10}H_{12}$ CLOSO

CLOSO





Nido Potta ion

* $C_2B_{10}H_{12} \xrightarrow[2\,MeOH]{NaOMe} Na^+[C_2B_9H_{12}]^- + B(OMe)_3 + H_2$

CLOSO

$\downarrow$ Base/Δ

$Na_2[C_2B_9H_{11}]^{2-}$

Serendipity ⇒ Luck by chance if something discovered.

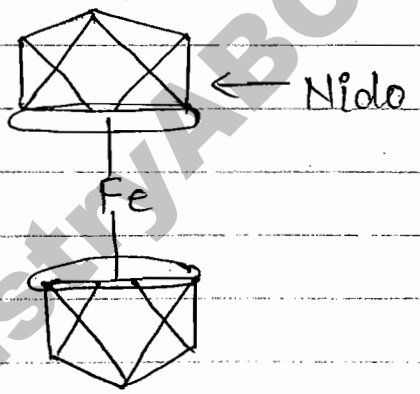
$C_2B_9H_{11}^{2-}$ ⇒ $(BH)_2B_9H_{11}^{2-}$

$B_{11}H_{13}^{2-}$ or $B_{11}H_{11}^{4-}$ Nido

* $C_2B_9H_{11}^{2-} \xrightarrow{FeCl_2} [Fe(C_2B_9H_{11})_2] + 2NaCl$

⇓

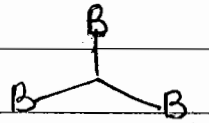
Potta Sandwich



STYX No.

It is a trick to learn the str. of Boranes.

S no. of  3c-2e⁻

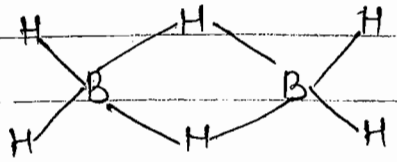
T no. of  3c-2e⁻

Y no of B—B 2c-2e⁻

X no of BH_2 units.

Boron in Boron clusters should be sp^3 i.e four co-ordinated.

(52)



S T Y X

2 0 0 2

M. Imp.

Boranes. STYX No.

1.	B_2H_6	Nido	$B_2 = 2+0$ Trick	2 0 0 2	
2.	B_6H_{10}	Nido	$B_6 = 4+2$	4 2 2 0	
3.	B_5H_{11}	Arachno	$B_5 = 3+2$	3 2 0 3	More H(11) so BH_2 unit 3.
4.	B_5H_9	Nido	$B_5 = 4+1$	4 1 2 0	Less H so BH_3 unit 0.
5.	B_4H_{10}	Arachno	$B_4 = 4+0$	4 0 1 2	

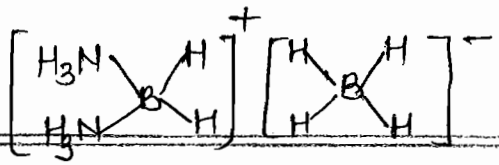
Q. Str. of B_5H_9

↳ Nido means one caped removed from CLOSO which is octahedral.

so on removal one L. from oct. ⇒ Geometry becomes sq. pyramidal so str. of B_5H_9 will be sq. py.

Q. Str. of B_4H_{10}

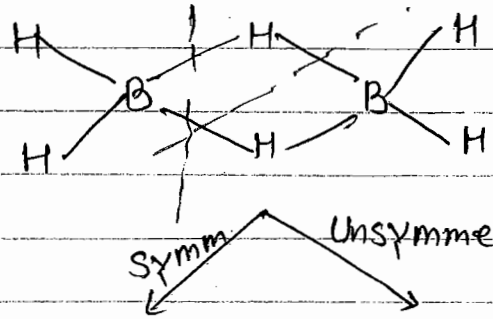
↳ ARACHNO ⟶ two capes removes from CLOSO (Oct) ⟶ One removal two twice lig from oct. ⇒ Sq. planar geometry



Properties :-

① $B_2H_6 + NH_3$ (excess) $\xrightarrow{100^\circ C}$ $B_2H_6 \cdot 2NH_3$ ionic

② $B_2H_6 + NH_3$ (excess) $\xrightarrow{\text{high temp.}}$ $(BN)_x$ polymer

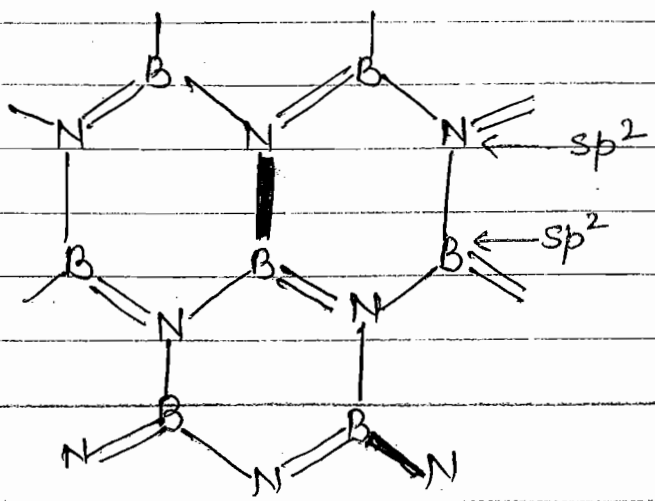


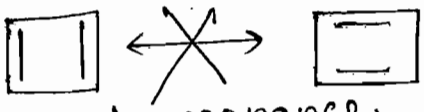
$BH_3 + BH_3$
Sym. cleavage by bulky reactant
Et_3N, Py

$BH_2 + BH_4$
Unsymmetric cleavage by small reactant
NH_3, RNH_2, R_2NH, Na, Li

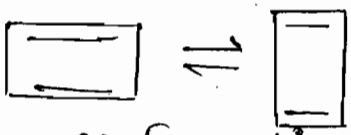
③ * $B_2H_6 + NH_3 \xrightarrow{450^\circ C} B_3N_3H_6 + H_2$

$(BN)_x$ ⇒ Boron Nitride or Inorg Graphite



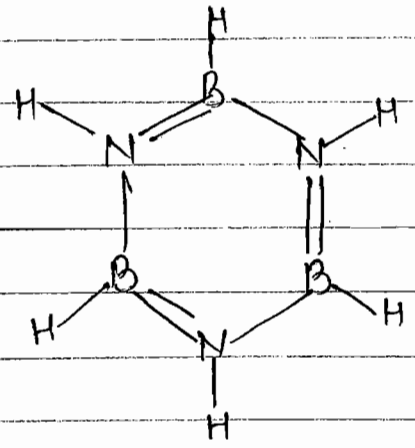


No resonance.



conformational isomers.

Ex: $B_3N_3H_6$ Borazine or Borazole or Inorg. Benzene.



Total atoms = 12

Total e^- = 30

C_6H_6

Benzene.

Total atom = 12

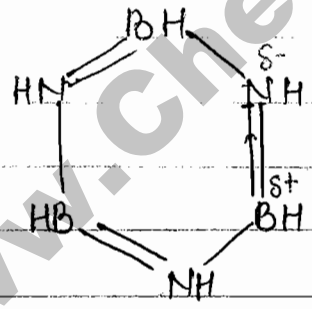
Total e^- = 30

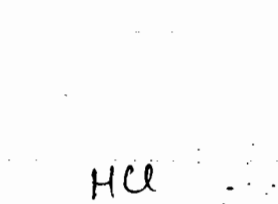
Isostructural.

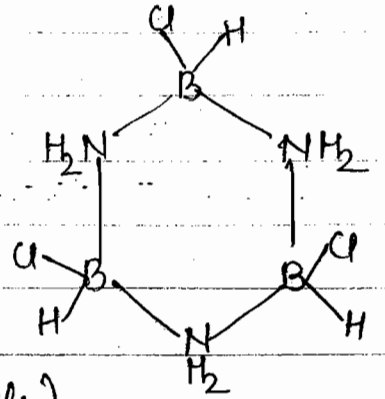
and also isosteres.

Isostere :- No. of e^- same & ~~str.~~ ~~also~~ Total atoms are also equal. (same).

* Borazine is less aromatic (almost negligible) than benzene.

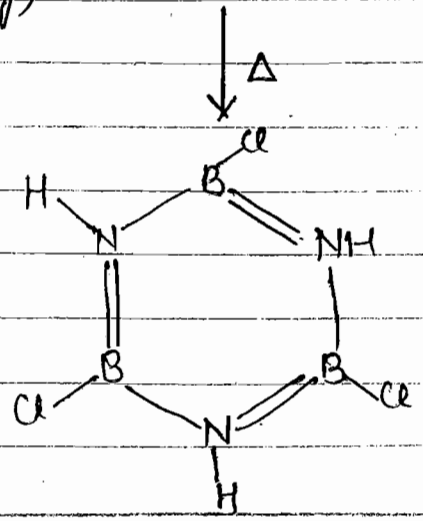






Less aromatic so addition Rex (Generally)

Q $B_3N_3H_6 \xrightarrow{HCl} A \xrightarrow{\Delta} B$



Q $B_3N_3H_6 \xrightarrow{CH_3OH} (A) \xrightarrow{\Delta} (B)$

Q $B_3N_3H_6 \xrightarrow{H_2O} B(OH)_3 + NH_3 + H_2$

* $C_6H_6 \xrightarrow{H_2O}$ No Rx.

Q $BCl_3 \xrightarrow[\Delta]{NH_4Cl} B_3N_3H_3Cl_3$

$B_3N_3H_3Cl_3 \xrightarrow{3\,MeMgBr} B_3N_3H_3Me_3 + 3\,Mg(Br)_3(Cl)_3$

$B_3N_3H_3Cl_3 \xrightarrow[\text{Reducing Agent}]{NaBH_4} B_3N_3H_6$

Lewis, acid, Base Character:-

It depends upon -

1) Availability of vacant d. orb of suitable energy.
2) Electronegativity.
3) Nature of solvent
4) Group attached with central atom.
5) steric repulsion

for Al.

L

↓ O, N donor atoms ↓ S, As donor atoms

$AlCl_3 > AlBr_3 > AlI_3$ (H.A. H.B.) $AlCl_3 > AlCl_3 > AlI_3$

for Ga,

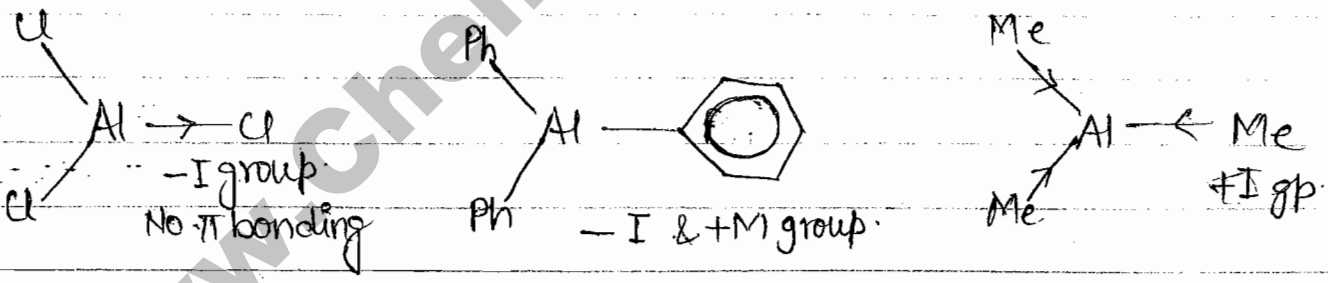
O, N: $GaCl_3 > GaBr_3 > GaI_3$ * S, As: $GaCl_3 < GaBr_3 < GaI_3$

S.A. S.B.

NET

Q Lewis acidic strength in Py solvent.

$AlCl_3$, $AlPh_3$, $AlMe_3$



→ $AlCl_3 > AlPh_3 > AlMe_3$

* $AlPh_3 > AlBr_3 > AlMe_3$

↑ less electronegative i.e. why less L.A than $AlPh_3$

Test of Boron Compounds:-

They are best tested by

Boron Comp. $\xrightarrow[\text{(or) } \Delta, \text{acid}]{\Delta}$ (A) gas $\xrightarrow[\text{(or) EtOH}]{CH_3OH}$ $B(OR)_3$ Ethyl Borate Green Colour

$\Rightarrow$ $BF_3 + HF \longrightarrow H[BF_4]$

$\downarrow H_2O$

$H[BF_3OH]$

Q BF_3 $H[BF_4]$ $H[BF_3OH]$ $H[BF_3\ddot{N}H_2]$ acid strength?

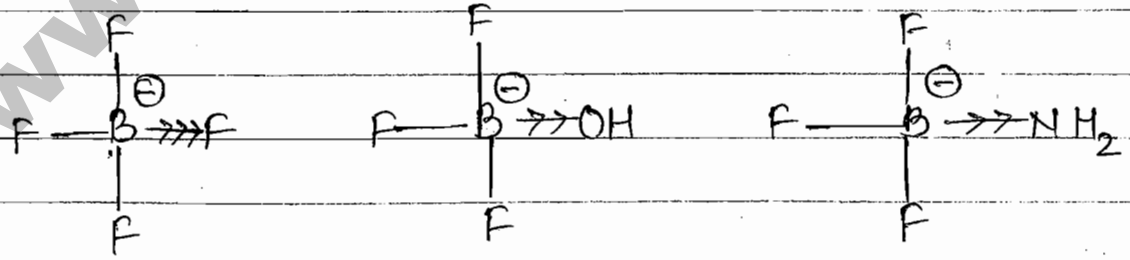
I II III IV

I — Lewis Acid

II, III, IV — Arhenious Acid

All Arh. Acid are Bronsted acid.

$-H^{\oplus}$ $-H^{\oplus}$ $-H^{\oplus}$



more stable conj base

Less stable conj base.

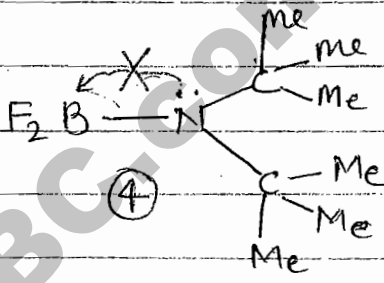
Acidic strength order I < IV < III < II

Q

F_2B-NH_2 ①

$F_2B-N(CH_3)_2$ ②

F_2B-N ③ (H, CH_3, CH_3, CH_3, H, CH_3) Loss of planarity but some π-bonding possible



④ Loss of planarity. No π-bonding.

i) Lewis acidic strength ?

ii) B—N bond rotation Energy Barriar?

iii) B-N B.O. ?

iv) B—N stretching freq.?

π bonding order ② > ① > ③ > ④

④ ← No π bonding

More π-bonding

π-bonding

⇓

More B.O.

⇓

More ν_{B-N}

⇓

Less Lewis acid.

No π bonding

⇓

Single bond only

⇓

Less B.O.

⇓

Less stretching frequency

⇓

More lewis acid.

i) Lewis acidic order ④ > ③ > ① > ②

ii) B-N bond rot. Energy Barriar order ② > ① > ③ > ④

iii) B-N B.O. ② > ① > ③ > ④

iv ν_{B-N} ② > ① > ③ > ④

Imp:

INERT Pair Effect :-

for p-block Elements.

		$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$
Lighter p-block		13	14	15
	2	B	C	N
	3	Al	Si	P
Heavier p-block	4	Ga $^{+1}_{+3}$	Ge $^{+2}_{+4}$	As $^{+2}_{+4}$
	5	In $^{+1}_{+3}$	Sn $^{+2}_{+4}$	Sb $^{+2}_{+4}$
	6	Tl $^{+1}_{+3}$	Pb $^{+2}_{+4}$	Bi $^{+2}_{+4}$

Sidgwick observed:

① Heavier element

- Higher O.S. (HOS.) — Due to involvement of both ns & np e⁻s
- Lower O.S. (L.O.S.) — Due to involvement of only np e⁻s

ns¹ e⁻ pair inactive on moving top to bottom ⇒ Inert pair Effect

② Observation

Group

① Stability of L.O.S. ↑

↓ ② Stability of H.O.S ↓

Eg. Stability order.

$Ga^{+} < In^{+} < Tl^{+}$

$Ga^{3+} > In^{3+} > Tl^{3+}$

$Ge^{2+} < Sn^{2+} < Pb^{2+}$

$Ge^{4+} > Sn^{4+} > Pb^{4+}$

$As^{3+} < Sb^{3+} < Bi^{3+}$

$As^{5+} > Sb^{5+} > Bi^{5+}$

③ I.P.E.

Starts from P.N. 4

Max. effect in P.N. 6

Eg.

$Tl^{3+} < Tl^{+}$

$Pb^{4+} < Pb^{2+}$

$Bi^{5+} < Bi^{3+}$

Note :- ① For P.N. 4 and Periodic No. 5 H.O.S Metal is more stable than L.O.S.

② For P.N. 6 H.O.S. Metals are less stable than L.O.S.

Explanation:-

Old View:- On moving top to bottom the penetration of ns e^- ↑, due to which $6s^2$ e^- pair is highly sorounded by f & d orb. & their bonding ability deraases. i.e. called as Inert pair Effect.

Modern View:-I.P.E mear (just) describe what is happening down the gp. i.e. inertness ↑, the actual ~~energy~~ reason is the bond energy of TlCl is more than that of $TlCl_3$ ↓ hence Tl^+ is more stable, infact in nature comp. of Tl^{3+} don't occur.

In other words we can say the energy required to unpair the ~~At~~ ns^2 e^- pair is more (Excitation energy) than the energy released when two extra bonds are form.

Application:-

$TiCl_3$ ⟶ $Ti^{3+} + 3Cl^-$

O.S. +3

↓

$Ti^+ + Cl_3^-$

↑

O.S. = +1 ✓

* $TlI_3 \longrightarrow Tl^{3+} + 3I^-$ ✗

↓

$Tl^+ + I_3^-$ ✓

* $GaCl_2 \longrightarrow$ Here Ga in +2 ox. state which is impossible it is may be in +3 or +1 O.S.

+1 +3

so $GaCl_2$ will be $(GaCl_2)_2 \Rightarrow Ga_2Cl_4$

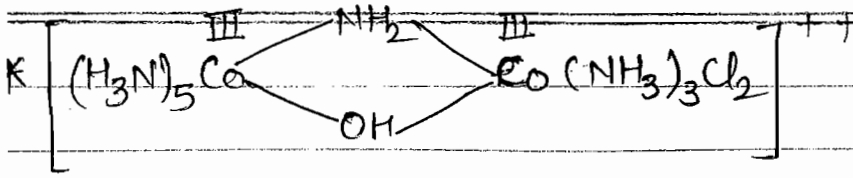
$Ga^{+}Cl$ ✓ $Ga^{+3}Cl_3$ ✓

* $\left[Br-\overset{I}{Tl}(Br)_2 - Br-\overset{III}{Tl}(Br)_2 \right]^{--}$

$2x = 6 + (-2) = 4$

$2x = 4 \leftarrow$ Oxidation No.

$x = +2$ can't be +2 on Tl only +1 or +3 so one Tl +1 state & other Tl in +3 O.S.



$$0 \quad x \quad -1 \quad -1 \quad +x \quad +0 \quad -2 = +2$$

$2x = +6$ ← Oxidation No.

$x = +3$ ← Oxidation state

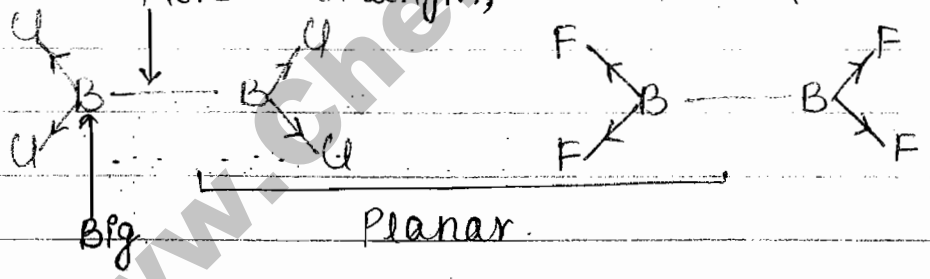
⇒ $CH_3 - CH_3$ Staggered ~~Elipsed~~ more stable due to less repulson b/w H' even it ~~is~~ is less symmetrical.

Small

⇒ $GeH_3 - GeH_3$ Elipsed more stable due to more symmetric, Here no H/H repulson.

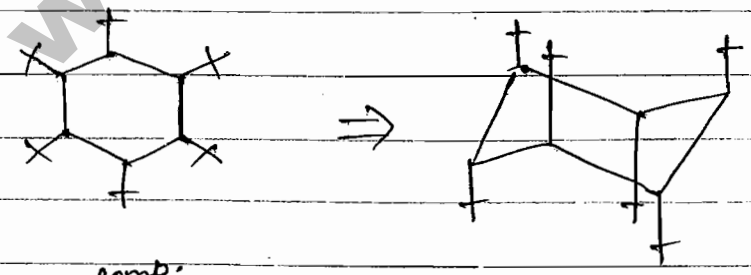
Big

⇒ More bond length, less H/H repulson.



Big

Planar.

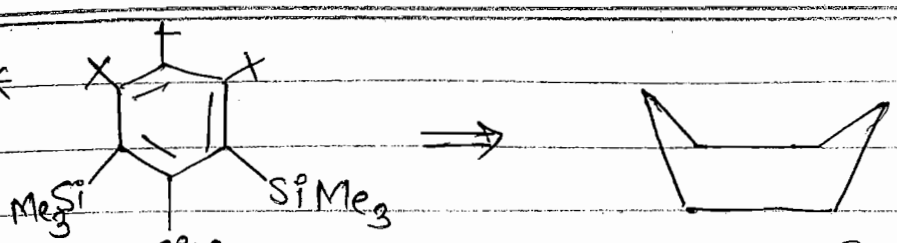
⇒ 

more molecular mass i.e. why solid state is found for this comp.

for this comp. t-Bu equatorial having less symmetry, less stable.

axial form is more symmetrical and more packing ⇒ more lattice energy ⇒ more stable

$I^{\ominus}$ is good reducing agent



Less stable

Boat form more stable.

* $Sn^{2+} \xrightarrow[-2e^-]{\text{Oxidn.}} Sn^{4+}$

Reducing agent

more stable

* $Pb^{4+} \xrightarrow[\text{Redn.}]{+2e^-} Pb^{2+}$

oxidising agent

more stable

* PbF_4

$PbCl_4$

$PbBr_4$

PbI_4

T.S. ↓

F^-

Cl^-

Br^-

I^-

Reducing power ↑

* $\overset{+4}{Pb}I_4 \longrightarrow \overset{+2}{Pb}I_2 + I_2$

$Pb + I_2$

Ionic bond is more stable than covalent bond.

NET Imp

* diamond having covalent bonds even it has more melting point in all the substance of world because it has 3D packing.

* B_2O_3 — $B(OH)_3$ ← Acidic
  Al_2O_3 — $Al(OH)_3$
  Ga_2O_3 — $Ga(OH)_3$
  In_2O_3 — $In(OH)_3$
  Tl_2O — Tl-OH

Acid strenth ↓

Base strength ↑

Stable only in +1

$\Rightarrow Al(OH)_3$ + HCl → $AlCl_3$ + H_2O

$Al(OH)_3$ + NaOH → $NaAlO_2$ + H_2O

Group No. 14 CARBON FAMILY

DIAMOND "

C Non metal
Si Semimetal
Ge Metalloid.
Sn, Pb] Metal

All type (4 type) element +nt.
⇒ Most Heterogeneous Group.

I.E. C > Si > Ge > Pb > Sn
↑ due to 'Ln' contraction.

Electronegativity C > Si = Ge = Sn < Pb
2.5 1.8 1.8 1.8 1.9
↑ due to 'Ln' contraction

Catenation Property:-
Catenation property is the ability of an element to show the self linkaging 'C' has the max. ability of catenation among all element, therefore it forms a no. of comp.
Reason :- * High Bond energy
* tnce of 2e⁻ or 3e⁻ or 6e⁻ in last shell.
*

'S' has the second position in periodic table for the catenation property.

C — C
Si — Si | catenation ↓
Ge — Ge ↓

Hyper valent 'C' spp:- forming multicentred bonding.

Spp.	C.N. of 'C'
CH_4	4
$\overset{\oplus}{C}H_5$, $Al_2(CH_3)_6$	5
$Fe_5C(CO)_{15}$	5
$(CH_3Li)_4$	7
$[Co_2(CO)_8C]^{2-}$	8

Allotropes of Carbon :-

Polymorphism :- Existance of a single spp. into more than one states having diff. physical and chemical properties. Both elements and compound shows this phenomenon, but in case of elements it is k/a Allotropy i.e. all allotropic form's are poly morphic form's but vice-versa is not true.

Chalk	Marble	Calcite
$CaCO_3$	$CaCO_3$	$CaCO_3$

Allotropes of Carbon

Amorphous	Crystalline
1) charcoal (Plant / Animal)	1) Graphite
2) Shoot	2) Diamond
3) Coke	3) Graphene
4) Coal	4) Fullerene
5) Lampblack	5) Lansodelite
etc.	6) Chaoite
	7) Charbon (VI) etc.

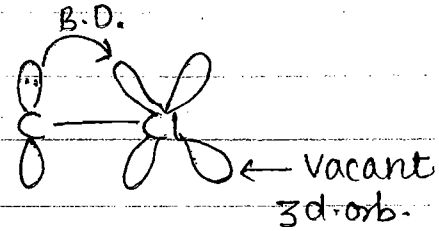
BACK DONATION :- Conditions :-

① The orbital size of donor & acceptor atoms should be similar.

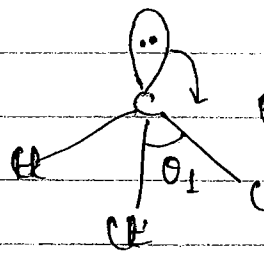
② Lewis acidic strenth & lewis basic strength should be high.

Acidic Strength :- $CHCl_3 \rightleftharpoons H^{\oplus}$

$CHF_3 \rightleftharpoons H^{\oplus} + CF_3^{\ominus}$

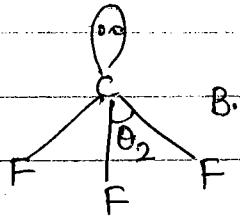


No Backbonding becoz F do not have any vacant orb.



Pyramidal

not planar becoz B.B. is not very effective becoz C has less e⁻ density (3Cl reducing the e⁻ density by -I gp)



Pyramidal

$\theta_1 > \theta_2$

* $CH_3-\overset{a}{C}H_2\rightarrow Cl \rightleftharpoons H^{\oplus} + CH_3-\overset{\ominus}{C}H\rightarrow Cl$ B.D. (very less only one Cl)

$CH_3-\overset{b}{C}H_2\twoheadrightarrow F \rightleftharpoons H^{\oplus} + CH_3-\overset{\ominus}{C}H\twoheadrightarrow F$

H^b are more acidic than H^a ⇒ due to less no. of Cl atoms.
B.D. is not very effective but -I effect is dominant.

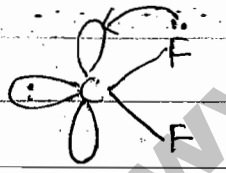
* $CH_3Cl < CH_3F$

* $CH_3\twoheadrightarrow CF_3 \rightleftharpoons H^{\oplus} + \overset{\ominus}{C}H_2-CF_3$ No. B.D.
More acidic

* $CH_3\rightarrow CCl_3 \rightleftharpoons H^{\oplus} + \overset{\ominus}{C}H_2-CCl_3$ No B.D.
Less acidic

⇒ $:CF_2 > :CCl_2 > :CBr_2 > :CI_2$

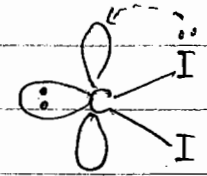
B.D. ability ↓, Stability ↓



More back donation.
2p-2p- overlapping.

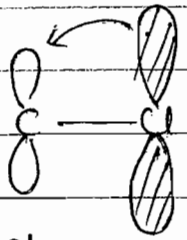
B.D = Back Donation

singlet carbene

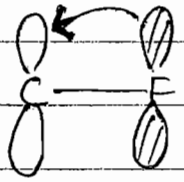


Very less back donation
2p - 5p overlapping.

* $\overset{\oplus}{C}Cl_3$ less stable than $\overset{\oplus}{C}F_3$



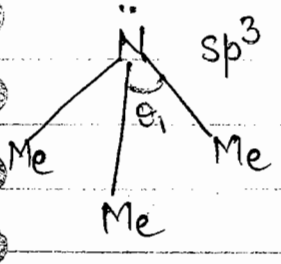
2p 3p
Less donation.



2p 2p More donation

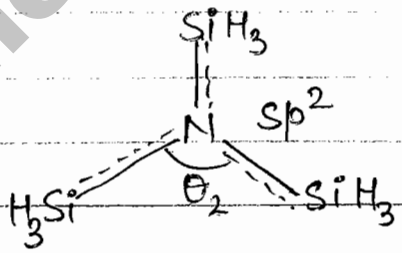
* $\overset{\oplus}{C}H_2 \rightarrow CCl_3$ more stable than $\overset{\oplus}{C}H_2 \rightarrow\rightarrow CF_3$

* $\ddot{N}(CH_3)_3$
No vacant orb. of 'C'



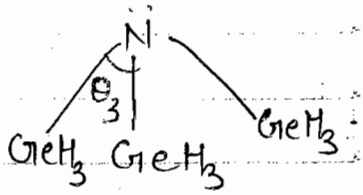
Pyramidal.

$\ddot{N}(SiH_3)_3$
Vacant orb. tnt on Si (3d)
B.D. possible



More B.D. l.p. not free
Here more e⁻ density at N (Si +I gp) i.e. why more B.D.

$\ddot{N}(GeH_3)_3$
Vacant orb. tnt on Ge (4d)
B.D. possible.



Not very much B.D.
Trigonal Pyramidal.

$\theta_2 > \theta_3 > \theta_1$

Lewis basic strength I > III > II

Q $\ddot{N}(CH_3)_3 + BF_3 \underset{}{\overset{K_1}{\rightleftharpoons}}$ (A)

$K_1 > K_2$

$N(SiH_3)_3 + BF_3 \overset{K_2}{\rightleftharpoons}$ (B)

No lp.

(A)		(B)
B—F		B—F
Bond order	<	Bond order
Bond length	>	Bond length
ν_{B-F}	<	ν_{B-F}

Q $\ddot{N}(CH_3)_3 + HCl \longrightarrow H-\overset{\oplus}{N}(CH_3)_3 Cl^-$

$N(SiH_3)_3 + HCl \not\longrightarrow H-\overset{\oplus}{N}(SiH_3)_3 Cl^-$

No lp.

$\downarrow$

$NH_4Cl + SiH_3Cl$

Q $H_3Si-OH \rightleftharpoons H_3Si-O^- + H^+$ More acidic

Silyl alcohol. more stable. (B.D.)

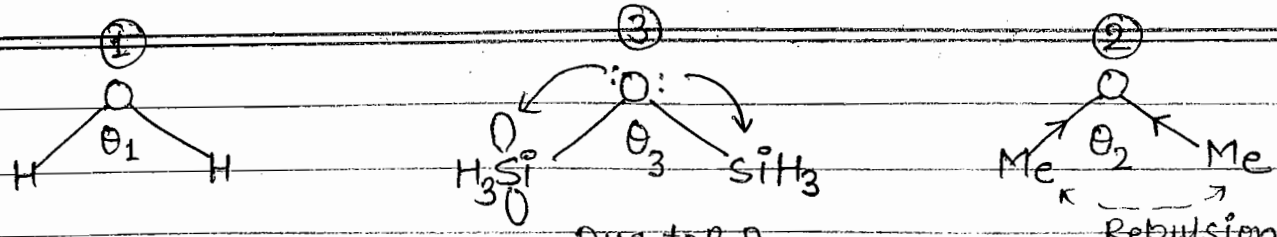
$CH_3-OH \rightleftharpoons CH_3-O^- + H^+$ Less acidic

Methyl alcohol. No B.D. Less stable

Acidic strength ?

Q Angle order ?, Basic strength order ?

H_2O, $(Me)_2O$, $(SiH_3)_2O$



Due to B.D.
angle increased.

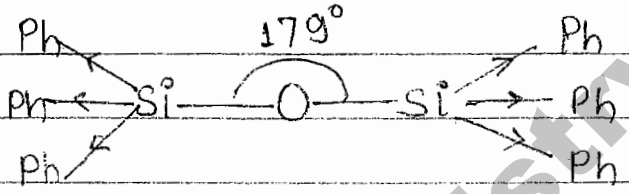
Angle order

$\theta_1 < \theta_2 < \theta_3$
105° 110°

↳ Hyb. $sp^2 - sp^3$

But in exam if sp^3 option is given then choose that one.

Basic order ② > ① > ③



More −I gp.
⇓
Si becomes very deficient of e⁻ so more lp donation by 'O' Angle increased and become 179°

Also $SiPh_3$ very large groups i.e. why more repulsion ⇒ Angle becomes 179°.

		Diamond like str.	Graphite like str.	Metallic str.
$p_\pi - p_\pi$ ability ↓ decreases	C	✓	✓	×
	Si	✓	×	×
	Ge	✓	×	×
	Sn	✓	×	✓
	Pb	×	×	✓

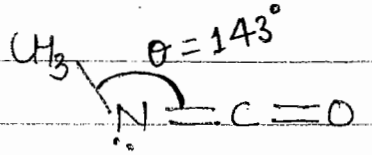
* α-Sn $\xrightarrow{13.5^\circ C}$ β-Sn $\xrightarrow{165^\circ C}$ γ-Sn

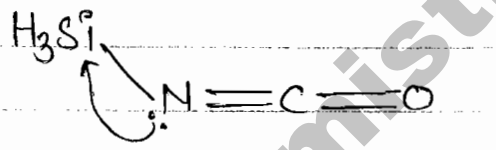
Grey — white

Tin plague
(Common in cold contries)

* MIC ⇒ Methyl Iso Cyanate

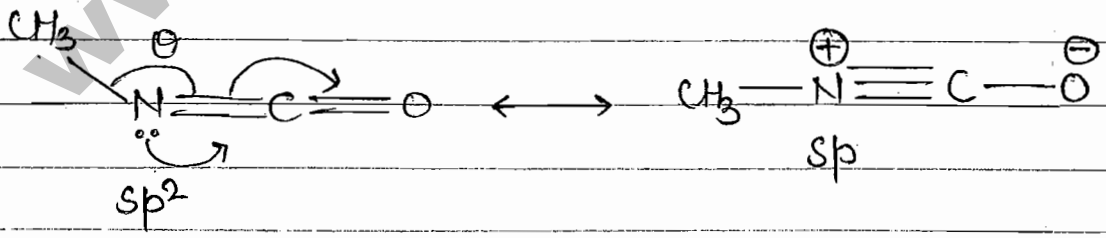
Bhopal Gas tragidy.

① 

② 

~~Syt~~ · Silyl isocyanate

sp hyb.
Linear.



↳ Due to resonance θ become 143° instead · 120°

Thermal conductivity not requires medium. (Sun heat comes on Earth without medium)
It may flow by Medium or without medium.

Allotropy of Carbon.

Diamond:-

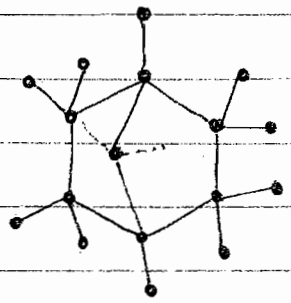
Carbon is sp^3 hyb., all the 4 valencies of 'C' are completely satisfied i.e. 4 e^- of 'C' are saturated. i.e. why diamond is diamagnetic & bad conductor. As the str. of diamond are highly compact i.e. it is why it is Hardest Known material. also diamond has very high thermal conductivity. C-C bond length in diamond is 1.54 Å i.e. C-C bond order is one.

Diamond is chemically inert. In it's giant form it has admantane like str. In the cavities of diamond some other element can be trapped or present giving colour to it. If Al is +nt that is Blue diamod (very costly).

The purity of diamond is expressed by unit Carate. 1 Carate = 0.2 g.

The biggest known diamond is Cullinin (3506 carate), Kohinoor (800 Carate)

In diamond 'C' form hexagonal rings.

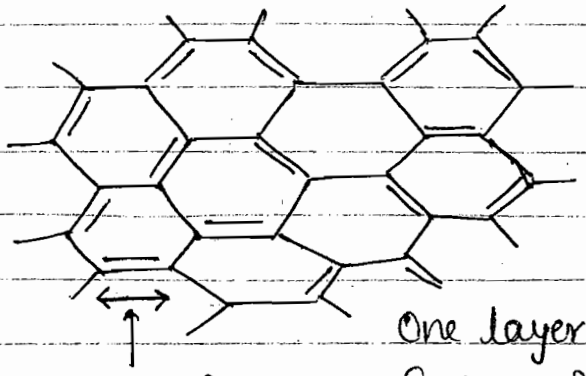


Diamond reflects all the insident light i.e. why they are very shining.

Diamond ⇒ 3 dimentional bonding

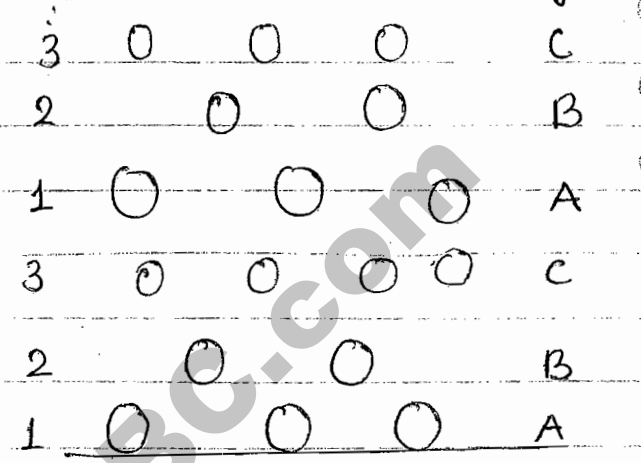
Graphite ⇒ 2 dimentional bonding

Graphite
- α — AB — AB — AB — Hexagonal packing
- β — ABC — ABC — ABC — Rhombic Packing

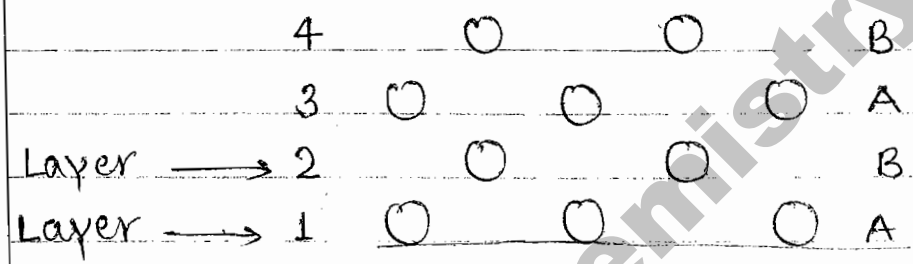


1.41 A°

One layer of Graphite



β-Graphite ABC type Layers



α-Graphite AB type layers

α Graphite ⟶ (Grinding) ⟶ β-Graphite

β-Graphite ⟶ (Temp. 1050°C) ⟶ α Graphite

पेंसिल में Graphite की layers होती हैं जो लिखने पर अलग होती जाती हैं क्योंकि Graphite की Layers के बीच Vanderwall force होता है जोकि Weak force है।

Core movie ⇒ diamond

Graphite is also known as Plumbago
Coal (कोयला) ⇒ Black Gold.

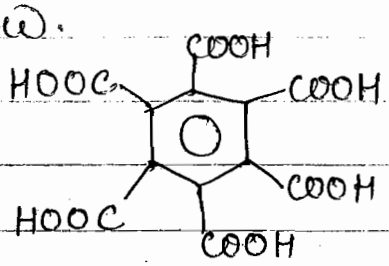
In graphite 'C' is sp^2 hyb. 3 e^- form normal single bonds and the fourth e^- of $2p_z$ orb. is delocalised over the entire layer, giving electrical conductivity but graphite is diamag. becoz fourth e^- get paired by virtue of π-bond formation. It's C-C bond length is 1.41 A°
In graphite Hexagonal rings forms layers and diff layers have fixed spacing (3.3 A°) These layers show diff. kinds of packing & diff. forms of graphite The two imp. forms are α & β in which β is more common and stable. In α form the packing is AB-AB - - AB type i.e Hexagonal packing. In β form the packing is ABC - - ABC - ABC type ie. Rombic packing. i.e. in α form every Ist and IIIrd layers are superimposed and in β-form Ist and fourth layers are superimposed i. e. ↵
the total distance b/w the super imposed layers is α and β are 3.34 X 2 and 3.34 X 3 respectivily.
Layers are bonded with weak Vanderwall forces therefore they are easily broken i.e why they are highly smooth hence used as lubricant.

Graphite + H_2O ⟶ Suspension (aqua deg.)
Graphite + turpentine oil/hydrocarbon oil ⟶ Colloidal solution.

The individual layers of Graphite are called Imp. Graphene (act as super conductor).

The density of dimond is more than Graphite.
Diamond is almost unreactive but Graphite is more reactive than diamond.
Graphite is thermodynamically more stable than diamond but the conversion of ~~graphite into~~ diamond into graphite is very difficult. enthalpy change for conversion is 1.9 Enthalpy.
The conversion don't take place becoz the activation energy for conversion very high. However graphite can be change into diamond by applied high temp. & high press. Value of temp. & press. can be minimise by catalyst (Ni) but such formed diamonds are ~~highly~~ tiny which can't use as ornament's but used in cutting & drilling machines.

Graphite show reactivity with $KMnO_4$, alkali but diamond don't show.

Eg. Graphite $\xrightarrow[\text{alkali}]{KMnO_4}$ 

Benzene hexa Carboxylic acid or Mellitic acid.

Diamond $\xrightarrow[\text{alkali}]{KMnO_4}$ No Rxn.

$\downarrow P_2O_5$

C_9O_2

Compounds of Graphite:-

Graphite forms comp. with O and fluorine i.e. called oxides & fluorides. also it forms lameller or inter calary comp.

Intercalary Comp.:- In b/w the layes of graphite, metal atoms can be trapped, such comp. are called intercalary comp. Metal may belogs to Alkali metal, d-block or f-block. Among s-block only alkalimetal forms stable intercalary comp.

$$C + M \longrightarrow C_{60}M \xrightarrow{M} C_{48}M \xrightarrow{M} C_{24}M \xrightarrow{M} C_8M$$

Graphite vapour

$M = K$

C_8K

Intercalary comp. has certain special properties.

1) They are very good conductor, although graphite & oxide or fluride are not conductor. but Graphite metal intercalary comp. are super conductor.
Eg. C_8K. (Super conductor)

The Increased conductivity is due to donation of e^- by metal to π e^- system of Graphite.
The intercalary comp. of graphite with alkali metal are superimposed i.e. A-A--A type but in case of trans. metal. they are alternate this is due to size effect of metal.

"Buckminster fuller" ⟹ Fullerene
Kroto, curl, Smalley Invent the Fullerene

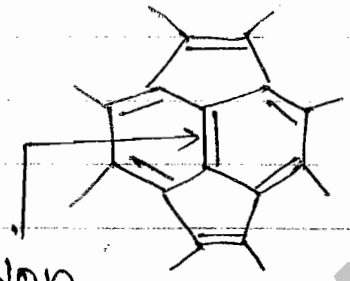
Conductivity of Oxide or Fluoride Graphite Less or non conductor becoz π e^- density withdrown by 'O' and 'F' atoms. due to which, Hexagon rings. bised towards 'F' or 'O' resulting destroy of aromaticity, consequence is non conductivity.

⇒ the intercalary comp. of Ln or Ac. 3e^- are donated by them but 1 e^- is transfered (back donated) from graphite ring to Metal to maintain its B.O. & stability.

FULLERENES → 12 pentagon, 20 Hexagon] for C_{60}

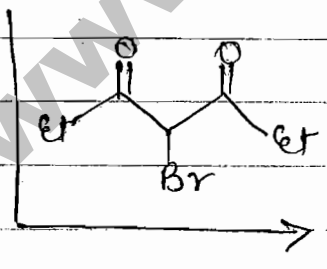
Graphite $\xrightarrow[\text{Beam}]{\text{LASER}}$ C_{60}, C_{70}, C_{80}, - - -

C_n n = Always even.

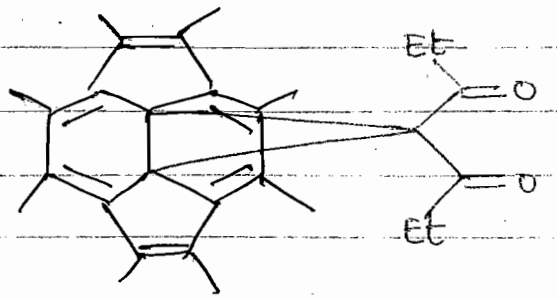


"a Fullerene part"

Non Huckle π bond (shows Addition Rxn)



BLing Rxn.



Addition Rxn.

12 pentagons in all fullerenes.

No. of Hexagon = $\left[\frac{n}{2} - 10\right]$ n = no. of C atoms in Fullerene.

Ex. C_{60}

$\left[\frac{n}{2} - 10\right] = \left[\frac{60}{2} - 10\right]$ = 20 Hexagons.

C_{70} $\left[\frac{n}{2} - 10\right]$ = 25 Hexagons
12 Pentagons.

C_{80} ⇒ 30 Hexagons, 12 pentagons.

Fullerene was discoved by Kroto - Smally & curl (Nobel

They discovered fullerene by the attack of LASER beam on graphite (1985) Fullerene has some special feature -

① The no. of C atoms are even.

② No. of pentagonal rings and hexagonal rings remain fixed. Hexalgonal rings are surroundend by penta- as well as Hexagonal. but penta gonal ring surrounded of only by Hexagonal rings.

③ Pentagonal Ring = 12 for C_{60}, C_{70}, C_{80}. but Hexa- gonal rings are not same, can be calculated by $[n/2 - 10]$

	pentagonal	Hexagonal.	Faces.
C_{60}	12	20	= 32
C_{70}	12	25	= 37
C_{80}	12	30	= 42

Huckel Rule upto 32°C ⟹ 4n+2 Aromatic
4n Antiaromatic

Huckel Mobius Rule After 32°C ⟹ 4n+2 Antiaromatic
4n Aromatic

4) The str. of C_{60} is truncated icosahedral. The C_{60} units are arranged in CCP or BCC arrangement. The single C_{60} unit is surrounded by other C_{60} unit giving a shape of icosahedral, therefore individual C_{60} is called truncated icosahedral.

5) Str. of these fullerene are similar with the famous "geodisc dome" -degsined by Buckminister fullerene. therefore they are named as fullerene. At present diff. fullerene are known with diff. no. of Atoms. fullerenes with less than 60 'C' are called Miniature bucky balls. & fullerene with more than 100 'C' are called giant bucky balls. fullerenes like C_{60}, C_{70}, C_{80} are called Soccur fullerene.

6) C_{60} fullerene give only one C^{13} NMR singnal. i.e. all the 'C' atoms are alike. but this fullerene have two type of bond length, it means there must be partial delocalisation. 5 Memb. rings are antiromatic & 6-memb. rings are aromatic. Overall fullerene suppose to be less aromatic & therefore they show addition Rxn. and also more reactive than graphite & diamond.

Graphite > diamond > Fullerene
stability order.

Diamond < Graphite < Fullerene
Reactivity order.

Fullerenes never show Substitution Rxn. even these are aromatic, ~~bec~~ because these comp. don't have any 'H' atom.

⇒Fullene is diamagnetic

Fullerene show Bling Rxn., Rxn. with OsO_4. F.

(7) Two fullerene units can be joint in a doumble shape manner, with the help of Bling rex. and so on. this method can be used in the preparation of bucky capsules called carbon nano tubes.

(8) Fullerene having more 'C' atoms show stereo isomerism. C_{70} fullerene is chiral while C_{60} achiral. C_{74} show 3 isomers. The C_{70} fullerene show 5 kinds of bond length. meaning it is less aromatic than C_{60}. The C_{70} fullerene show 5 C^{13} NMR singnals with intencity ratio 10:10:20:20:10

(9) C_{60} is the most common fullerene but C_{70} is more stable ~~althgho~~ although it is less aromatic. C_{60} fullerene is supposed to be a very high strained molecule, the decrease in strain in C_{70}, results in it's stability.

(10) Fullerene have particular cavity size therefore suitable size metal atom can be trapped. In these comp. Metal donates e^- to fullerene π-e^- system, making it negative.

(11) Fullerene also react with 'F' forming fluorides. but in these comp. 'F' atoms are bonded out side the ring.

(12) $C_{60}K$ fullerenes have K ion inside the cavity & the electrical conductivity increases. This is also used as superconductor like C_8K.

(13) Smaller fullerere are soluble in nonaqueous & Non polar solvent like benzene.

β-Boron ⟹ One unit have 105 Boron atoms

Black 'P' and Graphite are good conducter though they are non-metal.

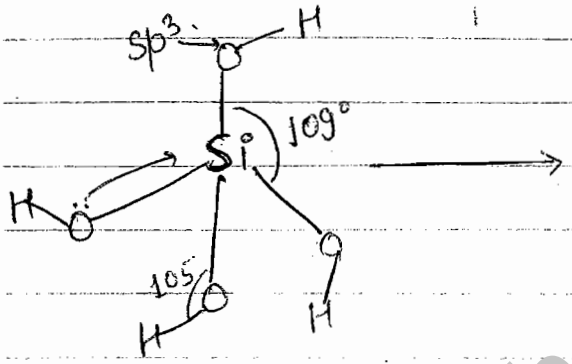
Lonsdeleite :- Cubic Wurtzite

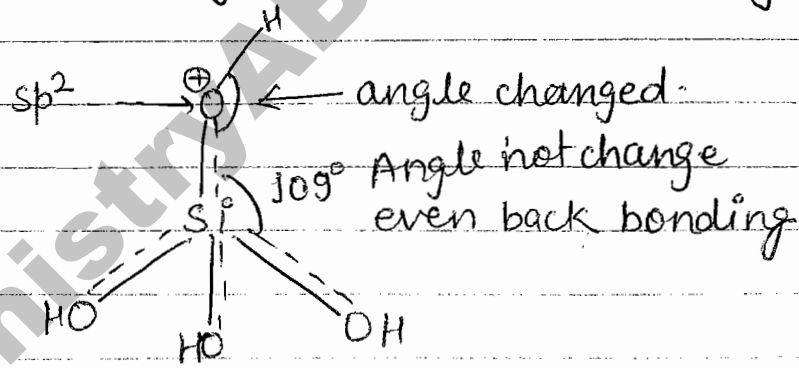
(1967)

SILICATES

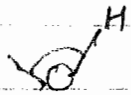
These are the metallic solids of silicic acid [$Si(OH)_4$]

Due to back donation the bond angle in $Si(OH)_4$ is changed. True of or false ?





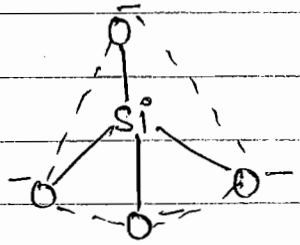
Angle changed.



* Si—O

↑ Polar Covalent bond.

* SiO_4^{4-} ion of Silicates



* More than 75% Earth crust formed by Silicates.

* O > Si > Al

← % in earth Crust

Blue diamond में cavity में Al Trap हो जाता है ⇒ Most costly diamond

Diamond str ⇒ Cubic sphere lite

Zircon = ज़रकाश (Radiation releasion)

Imp for GATE

Type of Silicates :-

Types of silicates depend upon the no. of oxygen shared.

① Orthosilicates / Neso silcates / Garnete silicates

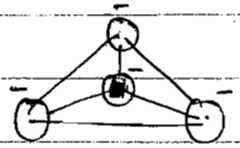
⇓

No 'O' shared

Basic unit $[SiO_4]^{4-}$ Eg. Zircon ⇒ $Zn^{4+}SiO_4^{4-}$

⇓

$ZnSiO_4$

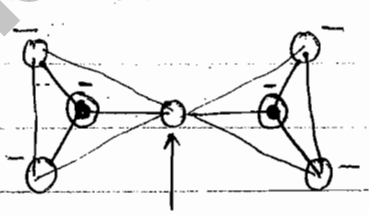


② Pyrosilicates (or) Soro silicates / Bow / Island silicates

⇓

Togather one 'O' is shared

Unit - $Si_2O_7^{6-}$



Shared 'O' no charge.

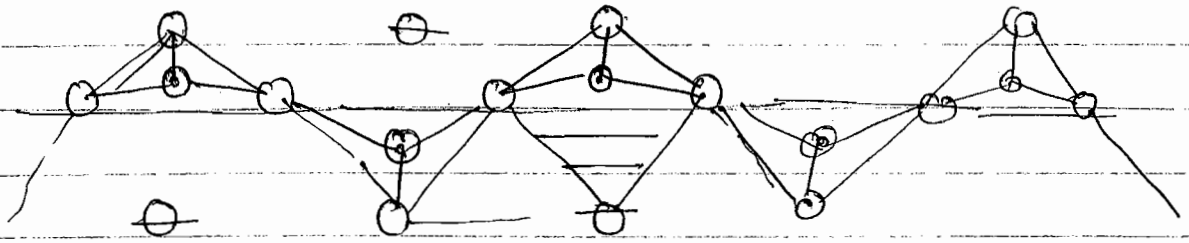
③ Chain Silicates ⇒ Two types

a) Single chain silicates :- Two 'O' shared ⇒ Pyroxenes.

General formula - $(SiO_3)_n^{-2n}$

Eg. $CaSiO_3$

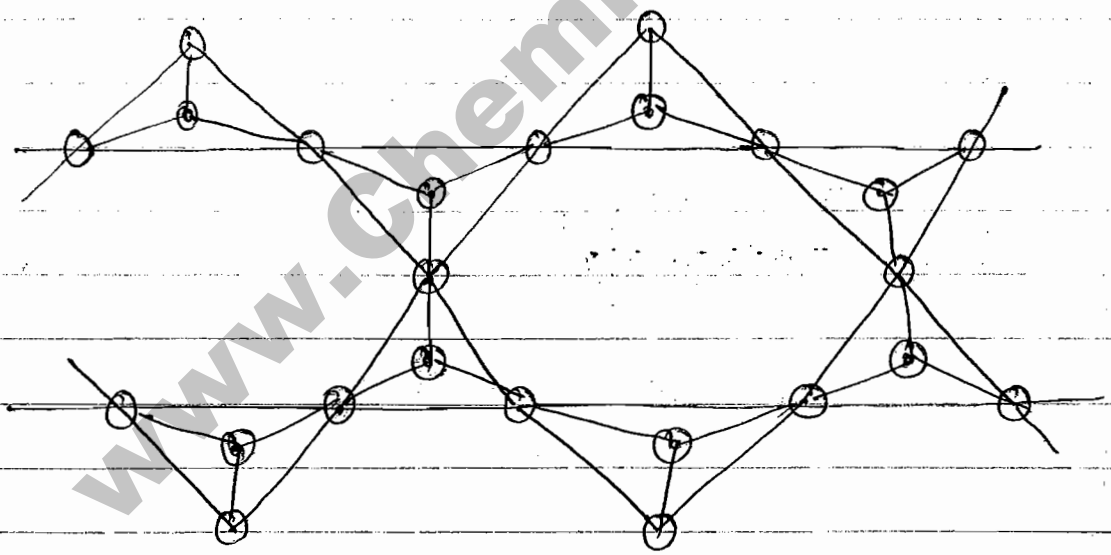
Na_2SiO_3 Water Glass



(b) Double chain silicates
- 50% units share two 'O' atom.
- 50% " " Three 'O' "

$\frac{2+3}{2} = 2.5$

Overall 2.5 'O' shared.



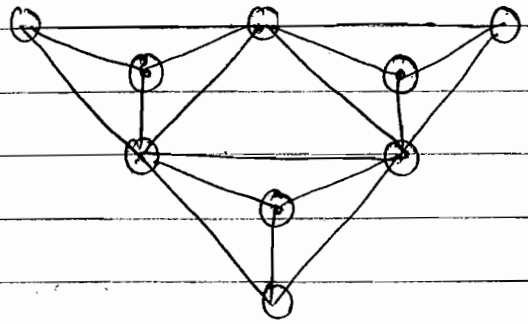
General formula ↓

Eg. $(Si_4O_{11})_2^{-12}$

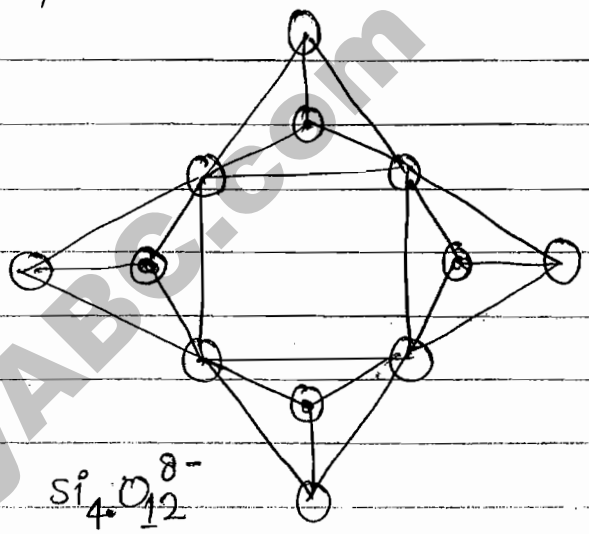
$(Si_nO_{11})_n^{6n}$

$Na_2 Fe_3^{II} F_2^{III} (Si_4O_{11})_2 (OH)_2$ Crocidolite

④ Cyclic Silicates :- Cyclic ring formed.

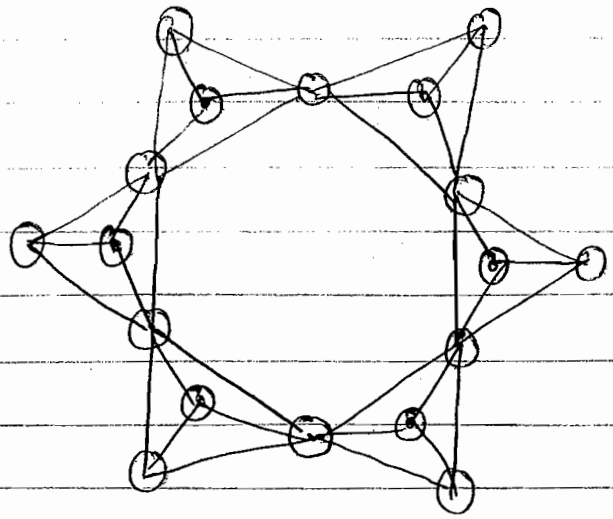


$Si_3O_9^{6-}$



$Si_4O_{12}^{8-}$

General formula $(SiO_3)_n^{-2n}$



$Si_6O_{18}^{-12}$

$Be_3Al_2Si_6O_{18}$

⇓

Beryl

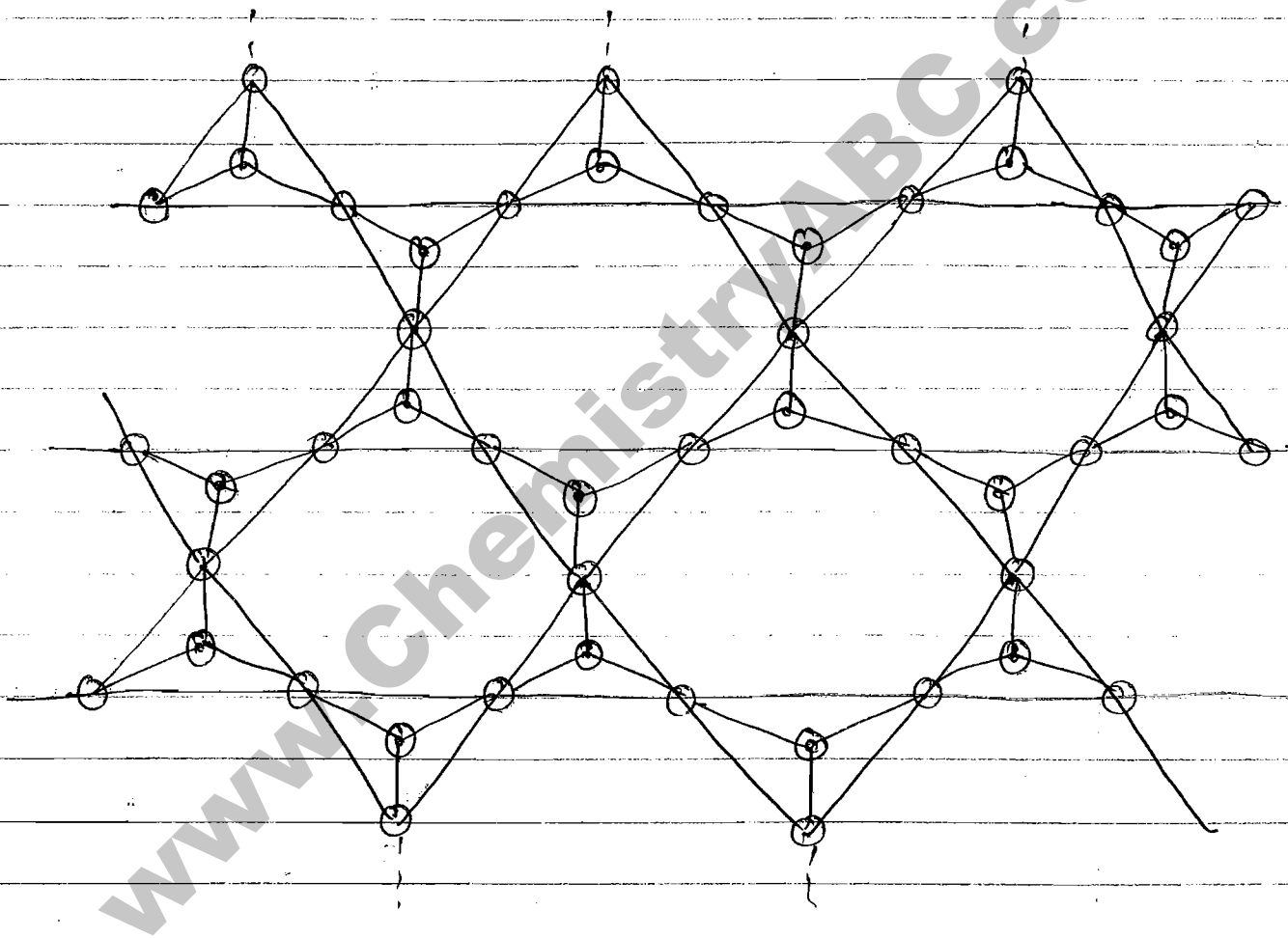
All types of ~~E~~Soils ~~are~~ have Silicates

Phyle = Planar.

5) Sheet Silicates / Phyllo Silicates

3 'O' atom shared.

General formula :- $(Si_2O_5)_n^{-2n}$



Plane sheets usually linked by -OH, H_2O & -ve charge is neutrilized by metal cations.

Eg ① Clay (~~चिकनी मिट्टी~~)

Kaoline (china clay)

Uses in ceramic, pottry industry

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ Kaolime.

In these silicates some silicon can be replaced by Al. such silicates called Allumino silicates.

② Talc:- It is also sheet silicates having Aluminium or Magnesium. In these silicates the sheets are attached with 'H' by OH group.

$[Mg_4(Si_2O_5)_2(OH)_4]$ Talk

③ Mica "Muscovite" Mainly found in India

⇓

Insulating malerial in which silicon atom replaced by 'Al'

$[Si_3AlO_{10}]^{5-}$ Mica (Muscovite)

✱

6) Three Dimentional / Tecto Silicates.

$(SiO_2)_n$ Neutral Silicates

These silicates have cavities / Tunnels. In these cavities Metal cations can be trapped.

Types:-

i) Feldspar

ii) Zeolites ⟶ $M[(AlO_2)_x(SiO_2)_y] \cdot zH_2O$ (Hydrated)

iii) Ultramarienes ⟶ $M[(AlO_2)_x(SiO_2)_y] \cdot anion$

Magma = लावा

* Feldspar found in Magma ⇒ Igniaus Rock.
* Zeolite & ultramarles ⇒ Alumino silicates
* Zeolite use in Aquaguard. It is also K/a Molecular Sieve. (छन्नी)
* Ultramarines is of beautiful coloured.

⇓

Eg. Lappis-Lazullie (लाजवर्द मणि)

↑ रूकमिणी पहनती थी

Colour of Ultramariene due to anion.

$Na_8[ALSiO_4]S_2$

$Na_8[AlSiO_4]Cl_2$ — These ions are responsible for colour.

$Na_8[AlSiO_4]SO_4$

Most Imp Si_3O_{11} is ?

How to learn General formula?

One silicon = 4 O'

3 Si = 12 O'

Here 11 O, means 1 O' shared.

⇓

Pyrosilicates

SILICONE POLYMERS

These are also k/a inorg. polymers

Preparation (3) steps.

step

1) Preparation of Silicon halides. with alkyl (or) aryl group:-

i) $SiCl_4 + Cu + CH_3Cl \xrightarrow{300^\circ C}$

(or)

$Si + CH_3Cl \xrightarrow[300^\circ C]{Cu}$

$\Rightarrow MeSiCl_3 + Me_2SiCl_2$ (major) $+ Me_3SiCl$

ii) $Si + CH_3Cl \xrightarrow[300^\circ C]{HCl/Cu}$

$SiCl_4 + Cu + CH_3Cl \xrightarrow[HCl]{300^\circ C}$

$\Rightarrow MeSiCl_3 + Me_2SiCl_2 + Me_3SiCl$ (Major)

iii) $MeMgCl + SiCl_4 \longrightarrow MgCl_2 + MeSiCl_3$

$2MeMgCl + SiCl_4 \longrightarrow 2MgCl_2 + Me_2SiCl_2$

$3MeMgCl + SiCl_4 \longrightarrow 3MgCl_2 + Me_3SiCl$.

Step II Hydrolysis:-

$Me_3SiCl + HOH \xrightarrow[-HCl]{} Me_3Si-OH$ monosilanol.

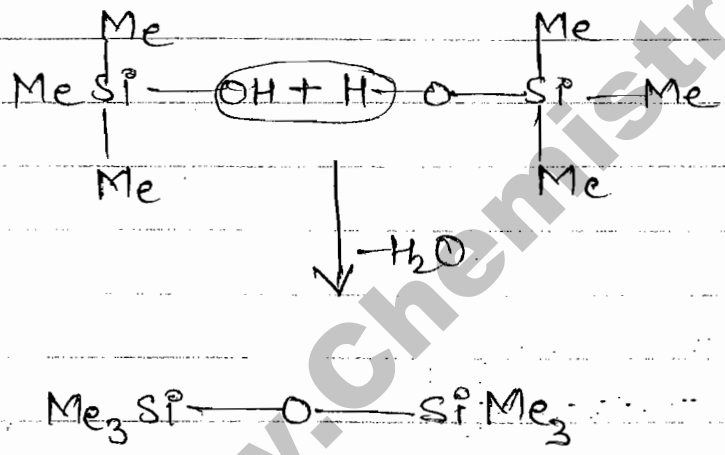
$Me_2SiCl_2 + 2H_2O \xrightarrow[-2HCl]{} Me_2Si(OH)_2$ Disilanol

$MeSiCl_3 + 3H_2O \xrightarrow[-3HCl]{} MeSi(OH)_3$ Trisilanol

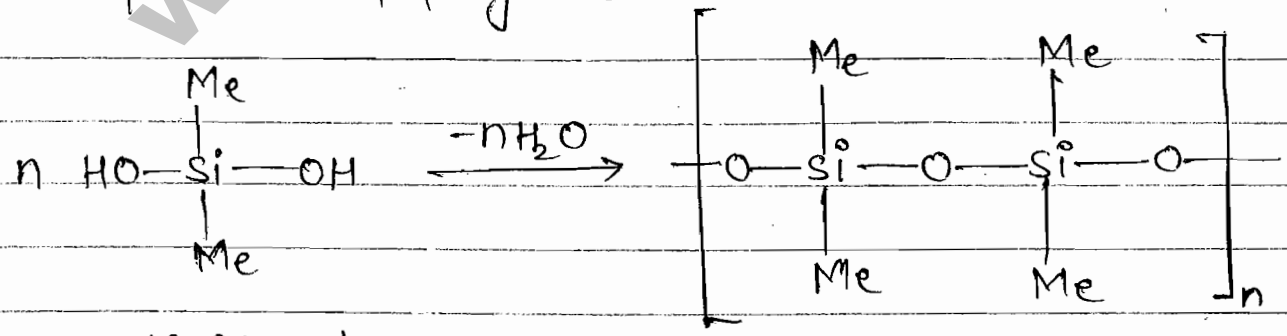
Step III

* Preparation Silicon ethers:-

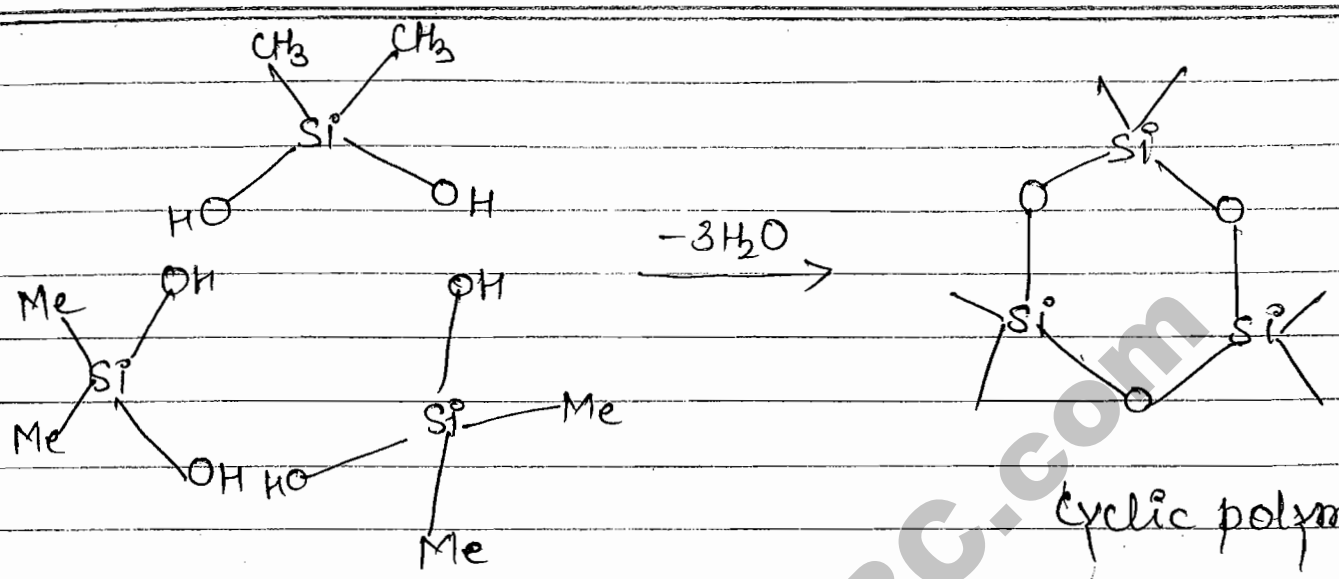
a)



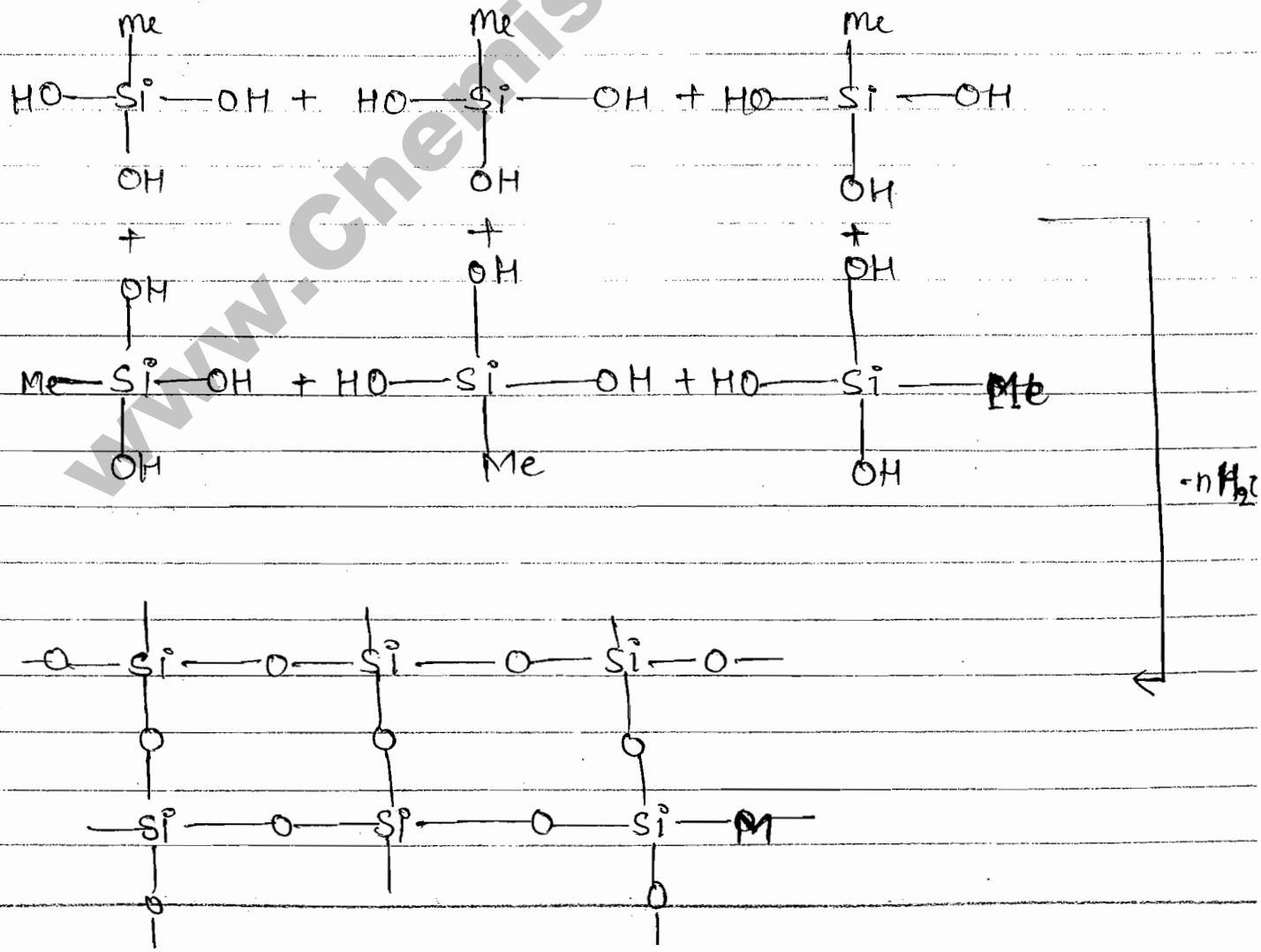
b) Preparation of polymers.



disilanol polymerisation.



c) Trisilanolpolymerisation :-



⇒ Silicons can be replaced by Al or P then they are called Aluminosilicones and phosphosilicones.

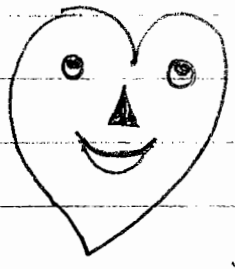
⇒ 'O' can be replaced by 'S' then they are called thiosilicones.

Properties:-

* Insulators
* Don't wet with water
* High resistant for thermal and electrical conductivity.
* Don't catch fire easily.

imp.

⇒ Silicon ethers very useful for making curtons. because they don't adsorbes dust particles i.e. why never become durty.



Angioplasty Pace maker made by silicon polymers.

Oxides:-

Carbon forms three types of oxides.

i) Monooxide $(C\equiv O)$

ii) Dioxide $CO_2, SiO_2, GeO_2, SnO_2, PbO_2$

$\longrightarrow$

T. stability $\downarrow$

$CO_2, SiO_2 \Rightarrow$ Acidic

$PbO_2 \Rightarrow$ Basic

Suboxide M_xO_y

if $x > y$ then suboxide

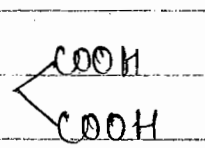
Ex. C_3O_2, C_5O_2, C_7O_2, C_9O_2, $C_{11}O_2$, $C_{12}O_9$

↑ Most stable

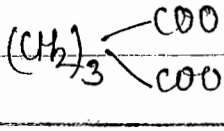
* N_2O Suboxide
* S_2O "

Oxalic acid.

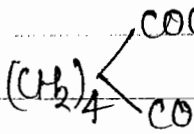
Malonic



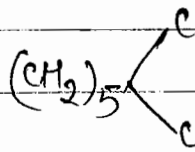
Succinic



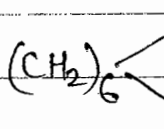
Glutaric



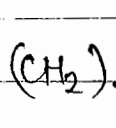
Adipic



Palmetic



Azetic



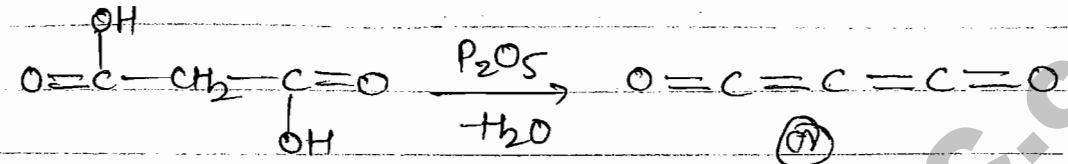
Suberic

Remember all these acids by this trick ↴

O My Sweet God Apple Pie As sweet

Oxalic | Malonic | Succinic

as Sugar

* 

(M)

C_3O_2

Carbon suboxide

* Red Lead ⇒ "Sindoor" ⇒ Minium

(M)

Plumboplumbic oxide

Pb_3O_4

$2\overset{+2}{PbO}$ $\quad$ $\overset{+4}{PbO_2}$

Mixed oxide

* $Fe_{0.93}O$

Fe^{++} & Fe^{+++} y.?

Non stoichiometric

(a) Interstetial comp.

let $Fe^{2+} = x$

$Fe^{3+} = 100 - x$

$Fe_{0.93}O$

$0.93x - 2 = 0$

$x = \frac{2}{0.93} = \frac{200}{93}$

$x \times 2 + (100-x) \times 3 = \frac{200}{93}$

Fe^{2+} x =

Fe^{+++} =

* $Pb_3O_4 \xrightarrow{HNO_3} \overset{+2}{Pb}(NO_3)_2 + \overset{+4}{PbO_2} + H_2O$

Freons:- "Chlorofluorocarbons"

C F C

C No.

Eg. CF_2Cl_2 Freons - 12 ← F No.

$CFCl_3$ " - 11

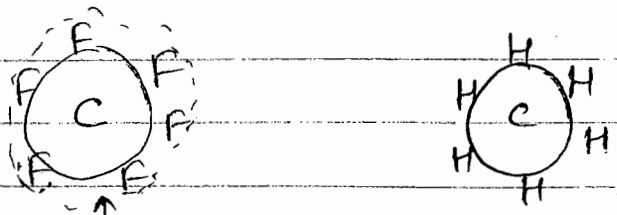
CF_3Cl " - 13

CH_3CF_2Cl " - 22

Freons ⇒ O_3 layer depletion (Free radical mechanism).

* $C_n H_{2n+2}$ hydrocarbon.
* $C_n F_{2n+2}$ Freon.

Ex. $C_5 H_{12}$ | Mol. mass ↑
$C_5 F_{12}$ ↓ but boiling point ↓ why?



e⁻ density outside
Polarisation easy
⇓
Weak London force
⇓
B.P. low

Neos ⇒ New Argos ⇒ Lazy. Krytos ⇒ Hidden, Stranger ⇒ Xenos

NOBLE GAS

He
Ne Rate of Adsorption ↓
Ar
Kr
Xe

Rn ← it is not found in air.

Air $N_2 > O_2 > Ne/Ar > CO_2$
76% ~23% ~1% ~0.003%

Q. Air → (Mg, N_2 absorbe) → ? → (Na, O_2 absorbe) → ? → (H_2O, CO_2 absorbe) → ? → condenced liq vol. ?

Air: solit N_2, O_2 Ne/Ar CO_2

? = N_2 -nt

? = O_2 -nt

? = CO_2 -nt

condenced liq vol. ? = Ne/Ar remaining which is 1% of air

1% of 60 lit = 0.6 lit

0K is not on temp. scale
zero ↑ ↳ Kelvin

* Noble Gases are Mono atomic proved by $\gamma = \frac{C_p}{C_v} = 1.66$
* They show London forces.
* Commonly K/a Aerogens

* Inert Gases are only He, Ne, Ar (only 3 are inert) doesn't form comp.
* Kr, Xe, Rn these 3 elements forms comp. so not Inert Gases.

Solubility in H_2O

He
Ne
Ar
Kr
Xe
Rn ↓

size ↑
London force ↑
b.p. ↑
Tendency of liquification ↑

solubility in H_2O ↑
Diffusion ability ↓

Ti ⇒ He = −236°C

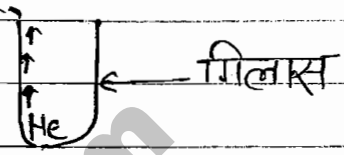
Ti ⇒ H_2 = −80°C

He - liquid. B.P. = 3.2 K

He-I ← → He-II

Below the B.P. (3.2 K) of He, as the temp. decreases two allotropic form of He are obtained called He-I & He-II. They have diff. quantum states. He II has certain special properties -

* It has almost very low viscosity, it means it is free flowing liq.
* It has tendency to move upword.
* It has very high conductivity more than 400-800 times better than silver.



* It has very low temperature, hence used as super coolant.
* It stored in magnetic field.
* It is found in air as well as sea bottom.

Imp He don't get adsorbe on charcoal.

COMPOUNDs of Noble Gases

Compounds before 1961

- In discharged tube
  He_2^+, Ne_2^+, HHe^+ ⇒ These are not true comp.
- Clatherates. (Cage comp. or Host Guest comp).

He_2^+ Ne_2^+ Ar_2^+, Kr_2^+

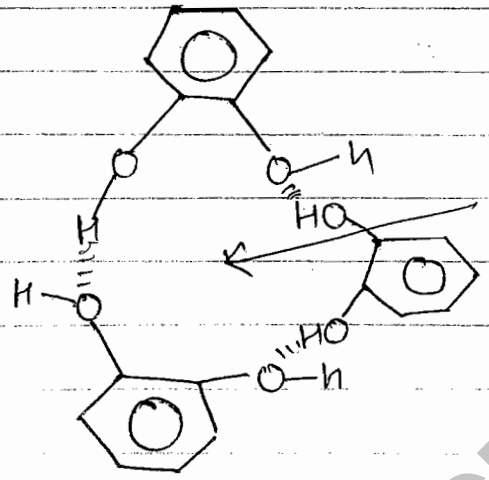
Rate of formation ↑

He
Ne
Ar
Kr
Xe
Rn

I.E. ↓

Clatherates are also not true comp. Actually when solvent are cooled for crystallization then they form cavities, in which noble gas atoms get trapped by the Vandewal forces. for eg: Catichol, Resorcinol, H_2O show these comp. formation.

Imp. He, Ne do not form Clatherates because they pass through cavity due to their small size.



Cavity (Ar, Kr, Xe trapped in this cavity as ~~Host~~ Guest).

Compounds After 1961:-

$Xe + PtF_6 \longrightarrow Xe^{+}[PtF_6]^{-}$ First Noble Gas Comp.

↑ Discovered by Neil's Bartlett
Nobel prize winner

The Ist I.E. of O_2 and Xe are comparible therefore Xe like O_2 can form comp. in which it show Ionization. from top to bottom I.E ↓. therefore Xe is most suitable for comp. formation.

grap.

Forms of Silica (SiO_2) :- Many polymorphic forms.

M. stable

α - Quartz ⇅ 570°C α - Tridymite ⇅ ~150°C α - Cristobolite ⇅ 270°C

β - Quartz ⇌ 770°C β - Tridymite ⇌ 1470°C β - Cristobolite ⇅ 1770°C

Liq. SiO_2

In α - quartz, the tetrahedra units are arrenged in Helical manner. Due to Helical str. α - Quartz is chiral.

$[Xe] + PtF_6$ —25°C→ $[XeF]^+ [PtF_5]^-$

$[Xe] + PtF_6$ —60°C→ $[XeF]^+ [Pt_2F_{11}]^-$ This was the actual formula presented by Bartlett

$[Xe] + F_2$ —Ni-vessel, ~300°C— 2:1 → XeF_2; 1:5 → XeF_4; 1:20 → XeF_6

Q. Why Xe forms comp. with O_2 & F_2 ?

A. F_2 & O_2 having very high e^- densities and high electronegativities therefore they can excite loosely bonded e^- of large xenon atom.

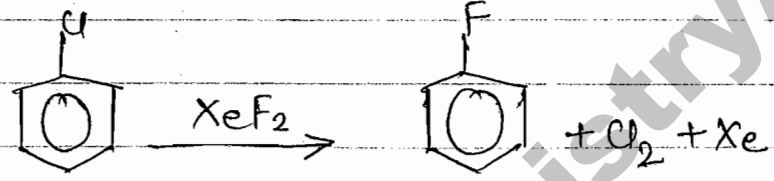
M. imp.

Properties and Structure :-

1) XeF_2, XeF_4, XeF_6

Act as fluorinating agent / Oxidising agent

Eg.



Ex. $CH_3Cl \xrightarrow{XeF_2} CH_2ClF + CH_2F_2$

2) Very reactive, orde is $XeF_2 < XeF_4 < XeF_6$

Reactivity of xenon fluorides $\propto$ no. of F atom.

3) $\overset{+2}{XeF_2}$ $\overset{+4}{XeF_4}$ $\overset{+6}{XeF_6}$ $\longrightarrow$

+ve charge on central Xe ↑

XeF bond length ↓

AsF_5 / SbF_5 ⇒ good F^- Acceptor

(SiO_2) Silica is most reactive with F & forms SiF_4

* $XeF_4 + AsF_5 \longrightarrow [XeF_3]^+ [AsF_6]^-$

* $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$

XeF_4: L. Base; SbF_5: Good L. Acid.

* $AsF_5 + XeF_2 \longrightarrow [XeF]^+ [AsF_6]^-$
  1 : 1

* $XeF_2 + AsF_5 \longrightarrow [Xe_2F_3]^+ [AsF_6]^-$
  2 : 1

* $XeF_4 + AsF_5 \longrightarrow [Xe_2F_7]^+ [AsF_6]^-$
  2 : 1
  Rxn prod. depend upon Reactant ratio

* $XeF_6 + AsF_5 \longrightarrow [XeF_5]^+ [AsF_6]^-$
  1 : 1

Hydrolysis :- Later on.

* $SiO_2 + XeF_6 \longrightarrow XeOF_4 + SiF_4$

* $Na_2CO_3 + XeF_6 \longrightarrow XeOF_4 + XeO_2F_2 + NaF$

* $NaNO_3 + XeF_6 \longrightarrow XeOF_4 + XeO_2F_2 + FNO_2 + NaF$

$Xe = 5s^2, 5p^6$

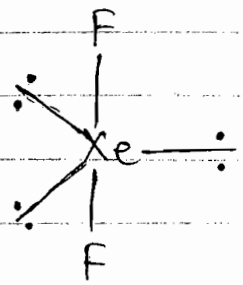
Structures:-

1) XeF_2

$Xe = 5s^2\ 5p^6\ 5d^0$

XeF_2 ↑↓ ↑↓ ↑↓ ↑ ↑ — — —

sp^3d



Geometry = TBP

Str/Shape = Linear

$5s^2, 5p^6, 6s^1$

I E.S.

~ 795 KJ/mol.

$5s^2\ 5p^5\ 5d^1$

I. E.S.

~ 981 KJ/mole

$5s^2\ 5p^4\ 5d^2$

II. E.S.

$5s^2, 5p^4, 5d^1, 6s^1$

II. E.S.

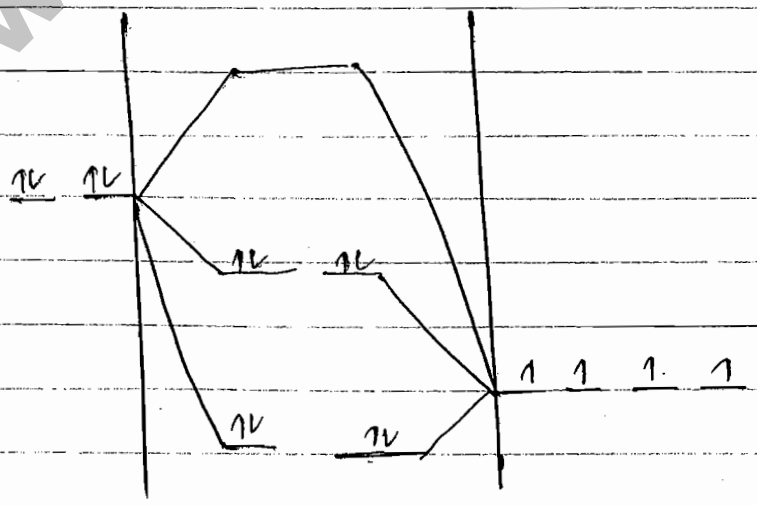
Total B.O. of $XeF_2 = \frac{2-0}{2} = 1$

B.O. = 1

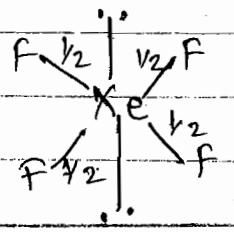
F —(1/2)— Xe —(1/2)— F

M.O. of XeF_2 see back.

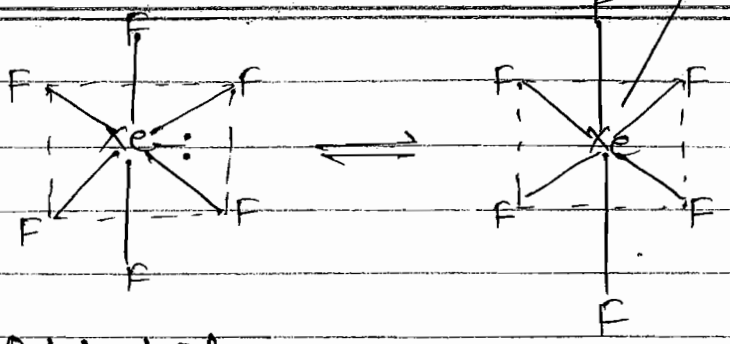
2) XeF_4



$B.O. = \frac{4-0}{2} = 2$



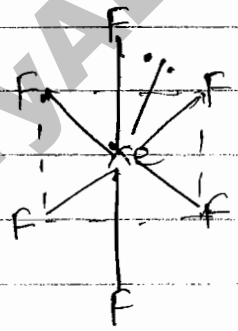
3) XeF_6



Octahedral
Stericallly inert
lone pair.

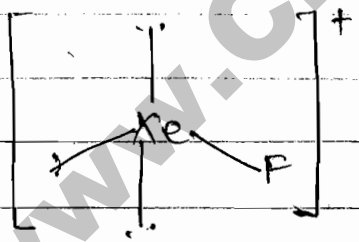
Monocapped Octahedral,
l.p. not stericallly inert

If Oh (Distorted) in option
then choose that one.



Distorted Oh.

4) $XeF^{\oplus}$



Geo - Td.
Shape - $[:\ddot{X}e—F]^{\oplus}$
Dumb-Bell or Linear

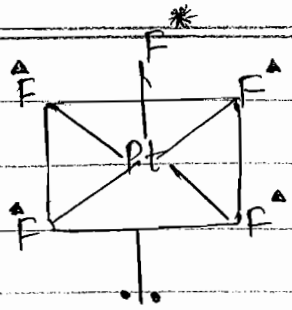
5) $[PtF_5]^-$ $\quad Pt(78) = 6s^1\ 5d^9$

$x = +4$

$Pt^{+4} = 5d^6, 6s^0, 6p^0, 6d^0$

$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \_\_ \quad dx^2-y^2 \quad \_\_ \quad \_\_ \quad \_\_$

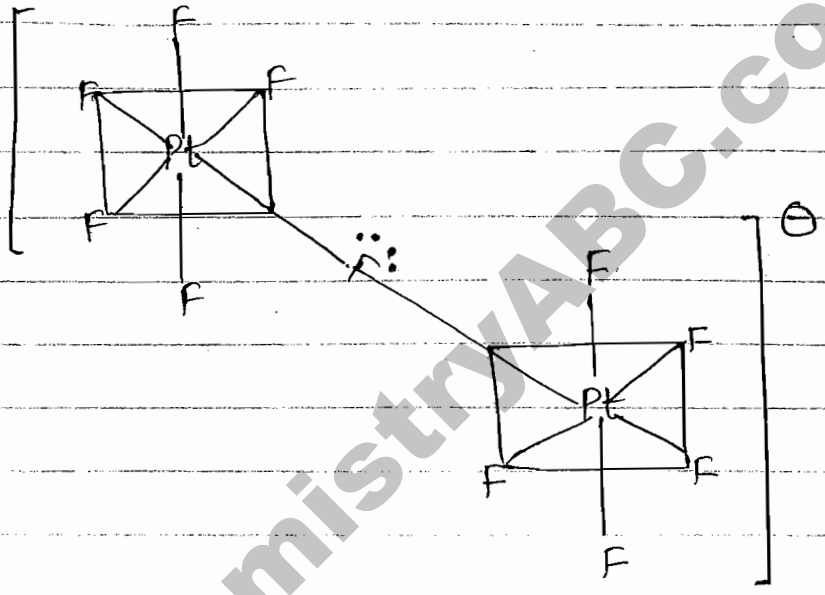
dsp^3



^{19}F-NMR - signal = 2

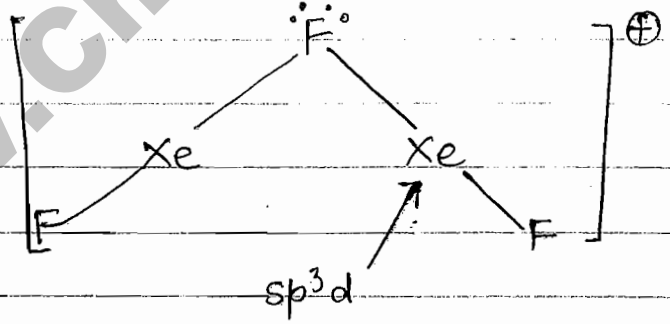
Squar pyramidal ~~str~~. Geometry more stable for Lower memb. of Group.

5) $[Pt_2F_{11}]^-$



M. Imp.

6) $[Xe_2F_3]^{\oplus}$

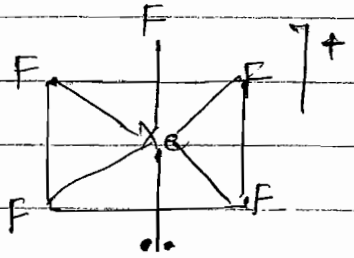


^{19}F-NMR = 2

Shape around F ⇒ Bent.

" " Xe ⇒ Linear.

7) $[XeF_5]^+$ sp^3d^2

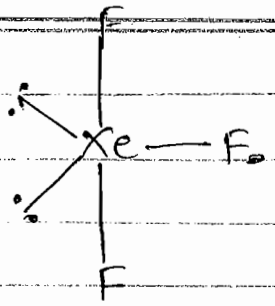


Shape sq. py.

^{19}F NMR = 2

Geo – Oh.

8) $[XeF_3]^{\oplus}$



Geo = sp^3d

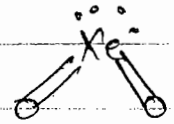
Shape ⇒ T shaped.

9) $[AsF_6]^-$ sp^3d^2 Oh.

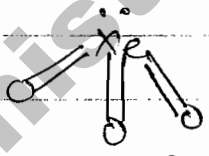
10) XeO_2 XeO_3 XeO_4

sp^3 sp^3 sp^3

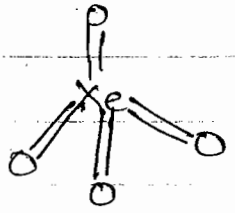
Td Td Td.



Shape Angular



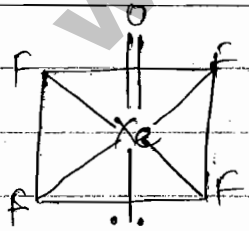
Pyramidal

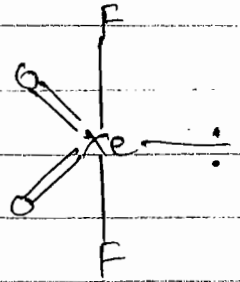


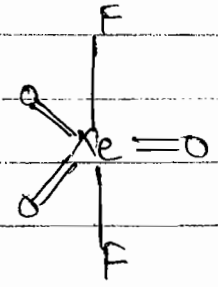
Td.

11) $XeOF_4$ XeO_2F_2 XeO_3F_2

sp^3d^2 sp^3d sp^3d







Geo = Oh Geo = TBP Geo = TBP

Shape = Sq. py Shape = See-Saw Shape ,,

Rxn. with Metal Fluoride:-

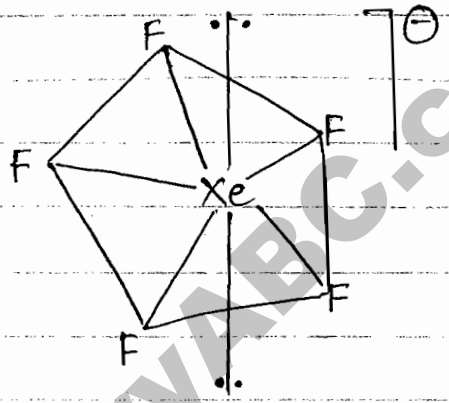
$$\overset{+}{M}\overset{-}{F} + XeF_4 \longrightarrow M^+[XeF_5]^{\ominus}$$

L.B. L.A.

Lux base Lux Acid

Geo = PBP

Shape = Pentagonal Planar



⇒ First comp. to have Pentagonal Planar shape.

$$MF + XeF_6 \longrightarrow M^+[XeF_7]^- \xrightarrow{\Delta} M_2[XeF_7]^{2-}$$

(M = Na, K, Rb, Cs) M = Na, K, Rb, Cs M = Rb, Cs, Na, K

$$M^+[XeF_7]^- \xrightarrow{\Delta} M_2[XeF_8]^{--}$$

M = Rb, Cs.

Most stable comp. of Noble gas family.

$[XeF_8]^{--}$

Sq. antiprismatic, sp^3d^4

Very big anion so l.p. sterically inert.

Pu^{+9} ⇒ Highest Oxⁿ· state among all elements

$[XeF_7]^-$ distorted dodecahedron.

Imp Lewis Acidic Strength:-

Xenon comp· are oxidising, fluorinating, L.Acid.

M.Imp· Trick:-

1) More the positive oxidation state, more will be acidic character for similar type of comp·

ex. $\overset{+2}{Xe}F_2 < XeF_4 < \overset{+6}{Xe}F_6$

Ex. $\overset{+4}{Xe}O_2 < XeO_3 < \overset{+8}{Xe}O_4$

2) For same type of comp· i.e. oxy fluoride -

if oxidation state same ⇒ more the no· of F atom, more will be L· acidity.

Ex. $XeO_3F_2 < XeO_2F_4$

For diff· Oxⁿ· state ⇒ More Oxⁿ· state, more will be L· Acidity.

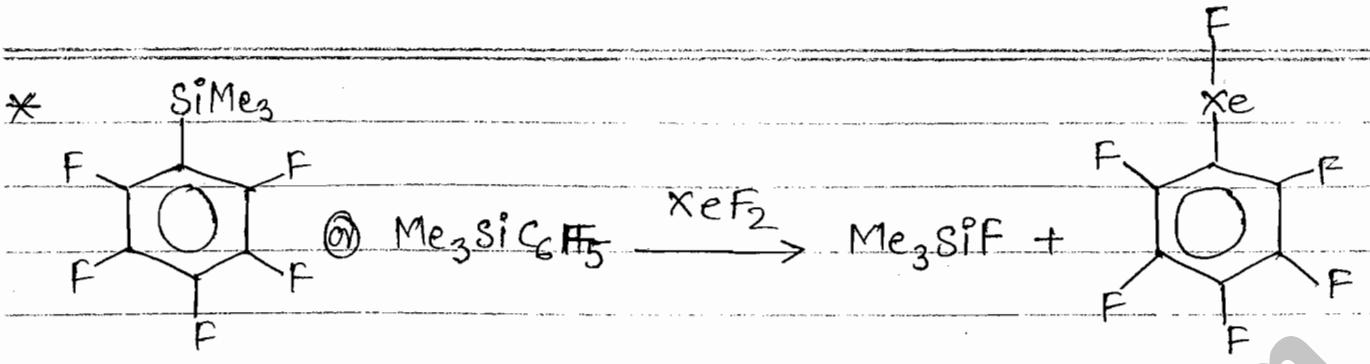
Ex. $XeOF_2 < XeO_2F_2 < \overset{+8}{Xe}O_3F_2$

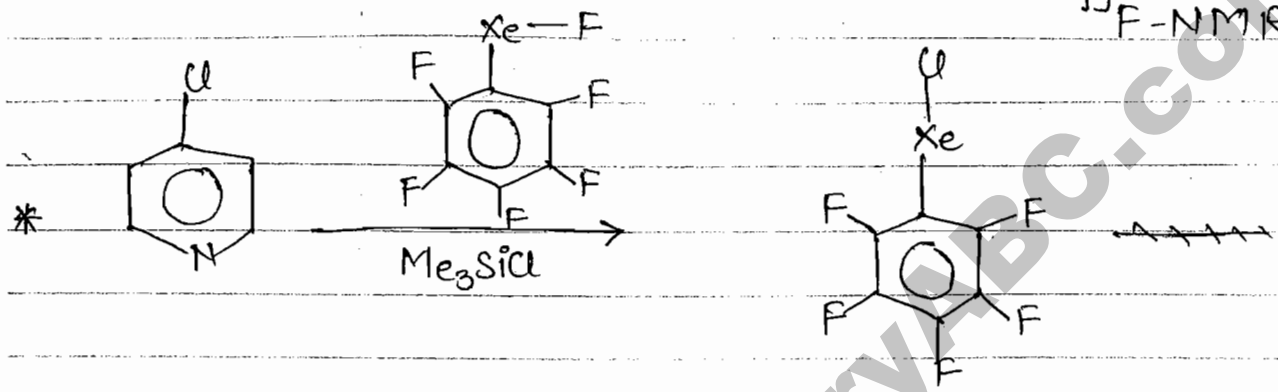
Note:- All these above comp· XeF_6 is most acidic & XeF_2 is least acidic.

Lewis acidic strength order:

$\overset{+6}{XeF_6} > \overset{+8}{XeO_2F_4} > \overset{+8}{XeO_4} > \overset{+6}{XeO_2F_2} > \overset{+6}{XeO_3} > \overset{+4}{XeOF_2} > \overset{+4}{XeO_2} > \overset{+2}{XeF_2}$

Tyeers.





Uses :-

* Helium :- 1) Super coolent (Cyrogenic agent)
2) Due to high upthreust it is used in Balloons and aeroplane tyers.
3) Sea - divers uses O_2 - He mix.

⇒ Bursting of blood vesceles by N_2 gas ⇒ Bending.

* Neon, Argon :-

1) They are used is Bulbs, CFL. Incandisent light (LED)
2) In making advertising bulbs ⇒ Neon Signal.
3) In making inert atmosphere used - Argon.
↑ for pericycle Rxn.

* Xe used in Rockets. $Xe \longrightarrow Xe_2^{\oplus} + e^-$

During Hydrolysis, the oxidation state of Central metal don't change

eg. $\overset{+4}{SF_4} \xrightarrow{H_2O} \overset{+4}{H_2SO_3}$ ✓ $\quad \overset{+6}{H_2SO_4}$ ✗

Imp.

HYDROLYSIS

$$4\,{}_{1}^{1}H \xrightarrow[\text{Fusion}]{\text{Nucleus}} {}_{2}^{4}He + 2\beta^{+} + 2\gamma$$

Fuel → Ash

Many mechanism are proposed for the hydrolysis of halides of main gp. (p-block mainly).

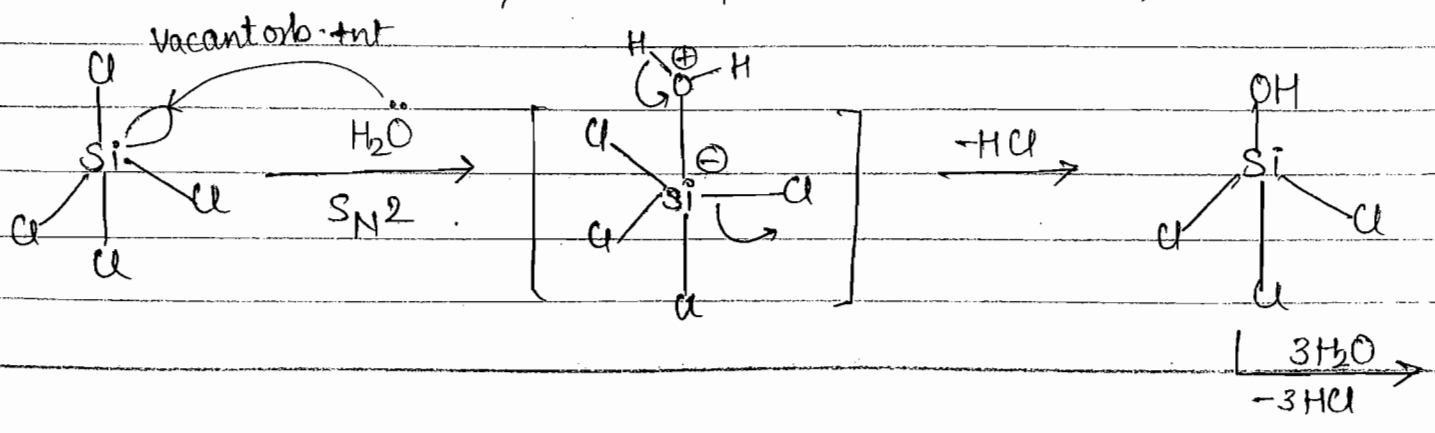
1) S_N1 Mech :- takes place under drastic condition

2) S_N2 Mech :- Most common and usually takes place for co-velent halides having –
Vacant orb. on central atom., +ve charge density on central atom.

3) Addition-elimination (Benzyne mech)

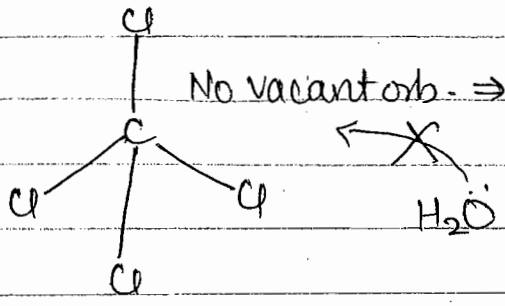
4) Other mechanism

Q $\overset{(+3)}{PCl_3} \xrightarrow{hyd.} \overset{+1}{H_3PO_2}$ ✗ , $\overset{+5}{H_3PO_4}$ ✗ , $\overset{(+3)}{H_3PO_3}$ ✓ , $\overset{+5}{H_4P_2O_7}$ ✗



14th Group.

→ $Si(OH)_4$ silicilic acid.

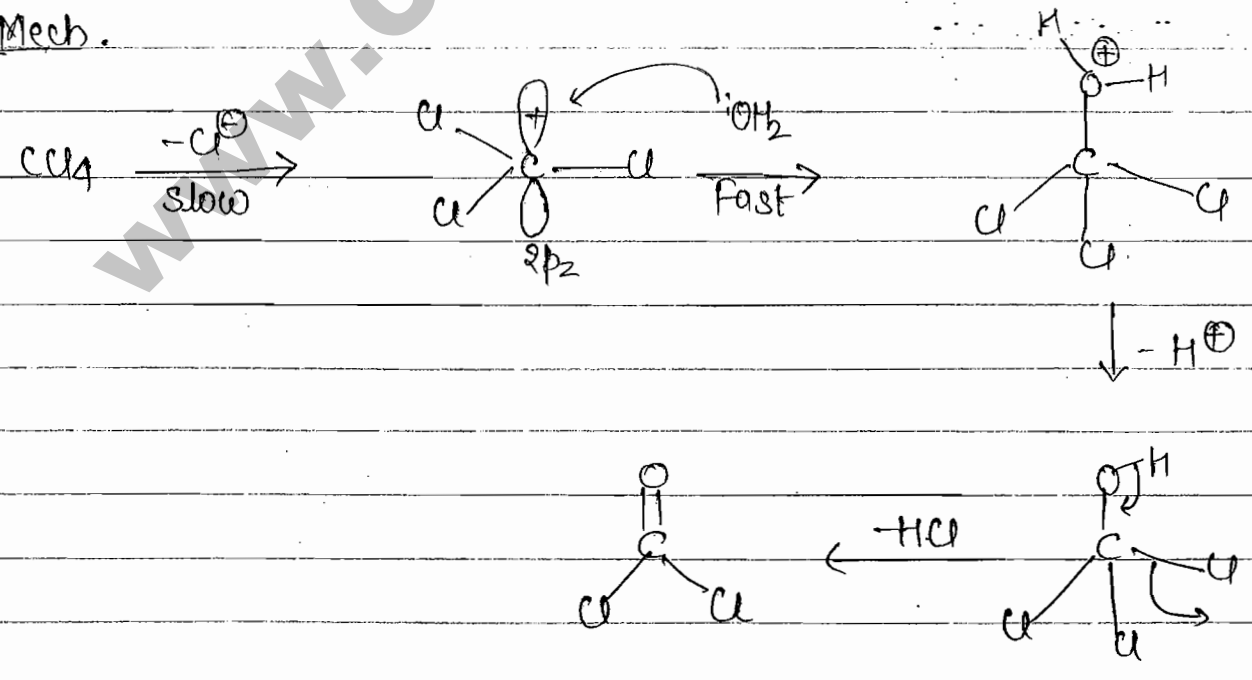


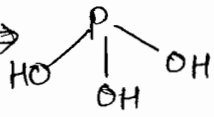
Under Drastic condition S_N1 takes place.

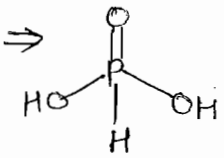
⇒ $CCl_4 \xrightarrow[\text{Steam}]{\text{Super Heated}} COCl_2 + HCl$

Phosgene
(or)
Carbonyl chloride

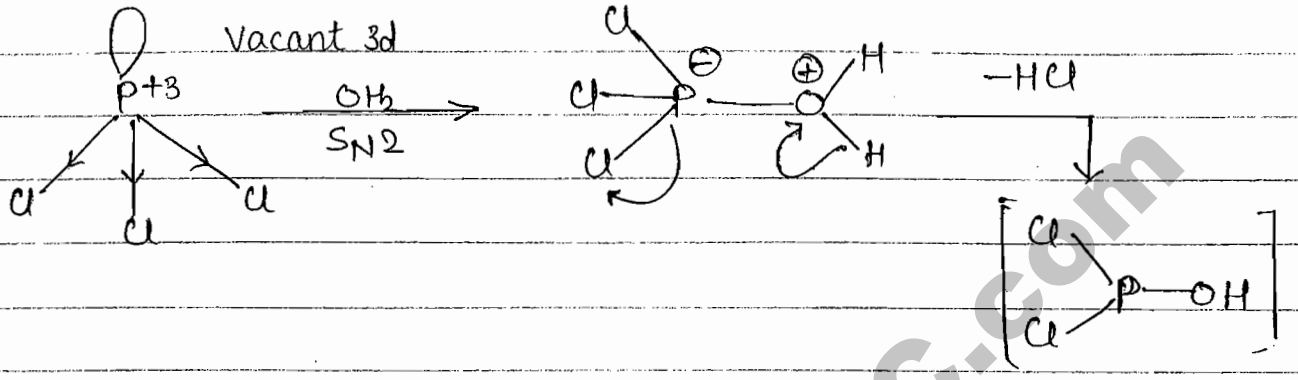
Mech.

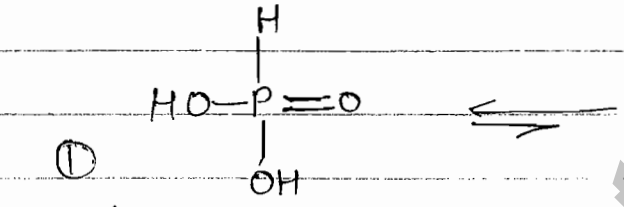


$P(OH)_3 \Rightarrow$ 

$H_3PO_3 \Rightarrow$ 

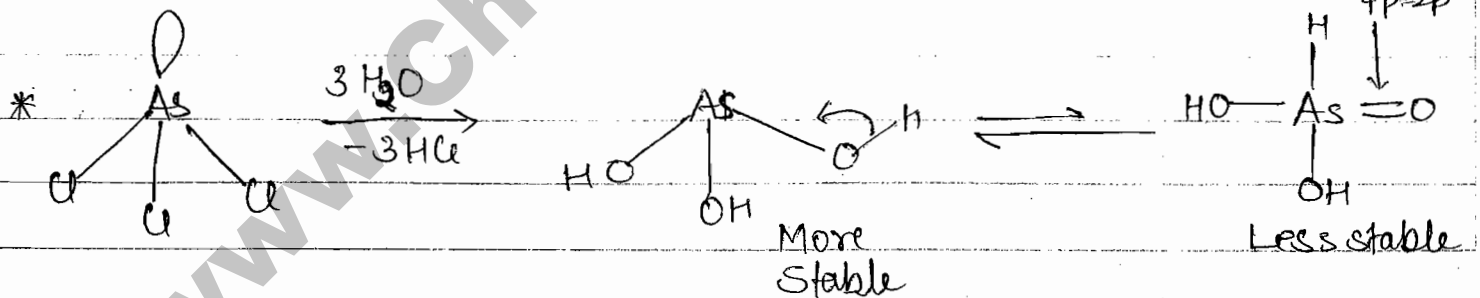
15th Group.

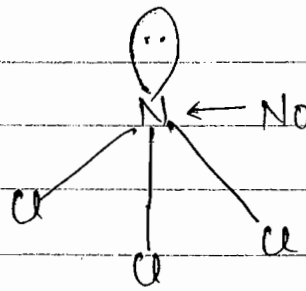
* 



① More stable ⟵ ⟷ ⟶ Less stable ②

If both option ① & ② given then choose ①

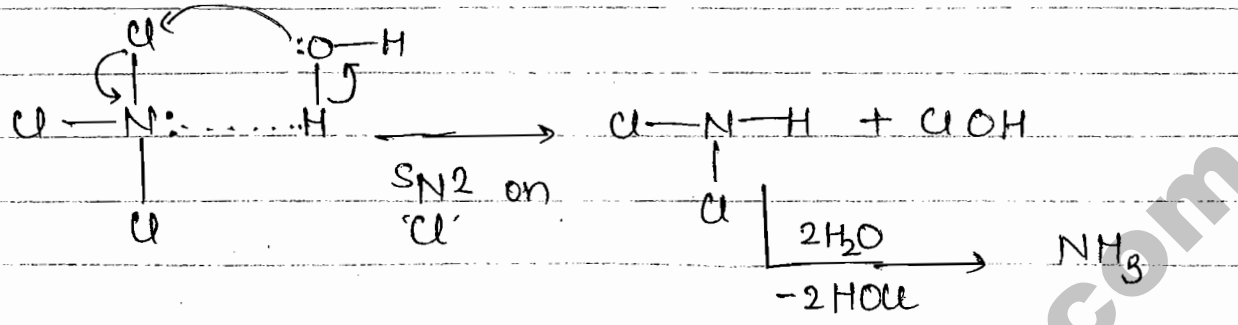
* 

* 

← No vacant orb. ⇒ No S_N2. on N

Electronegativity N = 3, Cl = 3.02 i.e. why $\overset{0}{N}Cl_3$ (N in zero O. state).

but Rxn. takes place due to 'H' bonding. (Semi S_N2 Rxn).



* $\overset{+3}{P}Cl_3 \xrightarrow{3H_2O} 3HCl + HO-\overset{H}{\underset{OH}{\overset{|}{\underset{|}{P}}}}(\overset{+3}{}=O)$ Same O. state ⇒ Hydrolysis

* $\overset{0}{N}Cl_3 \xrightarrow{3H_2O} 3HOCl + \overset{-3}{N}H_3$

Oxⁿ. state change ⇒ No Hydrolysis Rxn.

* $PF_3 + 3H_2O \longrightarrow$ No Rxⁿ.

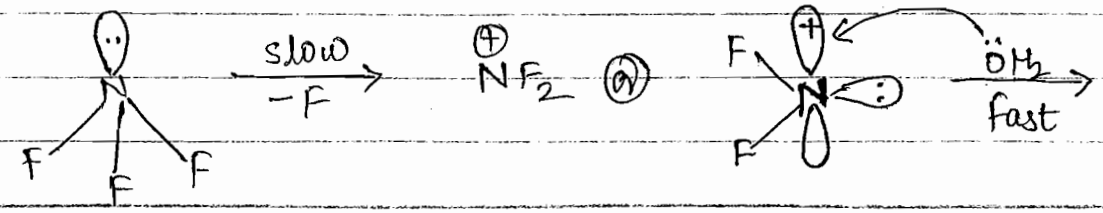
No leaving group. (P–F bond very strong)

* Rate of hydrolysis $PF_3 < PCl_3 < PBr_3 < PI_3$

P–F bond length increases.

good L.G.

* Hydrolysis of NF_3 under Drastic condition (S_N1)



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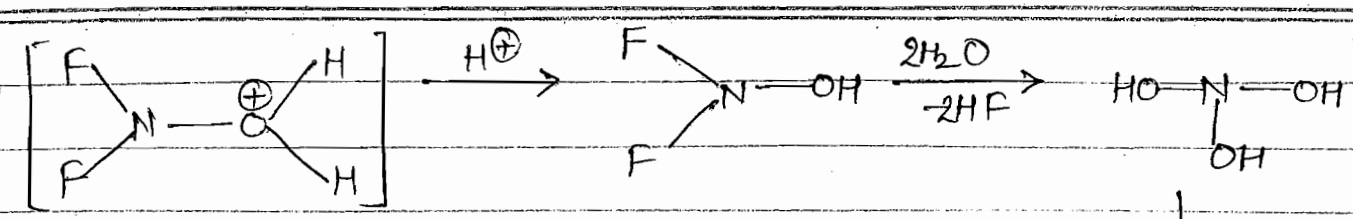
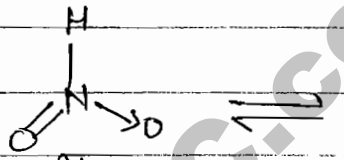
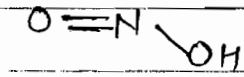


Non formed

H_2O



Nitro form



Nitrus Acid

*Thermal stability decreases:

- NF_3] Gas
- NCl_3] Natural explosive gas
- NBr_3, NI_3] Highly unstable

S_N2 (Hydrolysis)

- NF_3 ✗
- NCl_3 ✓
- PCl_3 ✓
- CCl_4 ✗
- $SiCl_4$ ✓
- $AsCl_3$ ✓

S_N2 Hydrolysis.

- SiF_4
- $SiCl_4$
- $SiBr_4$
- SiI_4

↓ T. S. ↓ Positive charge over Si ↓ Rate of S_N^2 Hyd ↓

S_N1 (Hydrolysis)

- CF_4
- CCl_4
- CBr_4
- CI_4

↓ Rate of S_N^1 ⊕ ↑ T. stability ↓

Acids of non metal

Hydra acid

Ex. H—N·

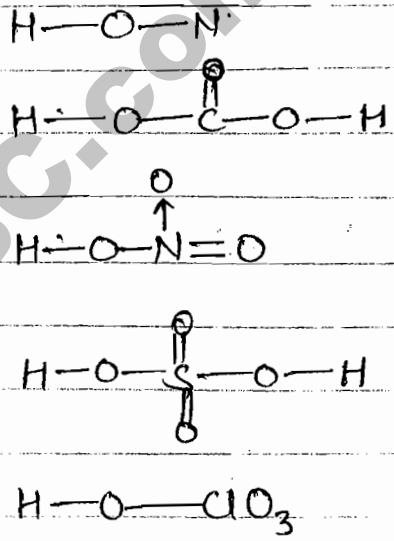
H—Cl

H—F

H—Br

Oxo acids.

Ex.



Generally oxoacid में Non metal के साथ 1 'O' double bond से साथ attach होती है।

M. imp.

Non-metal Elements	No. of -OH Hold by non-metal.
C	1 -OH, 2-OH
Si	4 -OH, $Si(OH)_4$
N	1 -OH, HO—N(=O)→O
P	1, 2, 3,
Cl	1 -OH
S	1 ~~OH~~, 2-OH

Br	1-OH
I	1-OH, 3-OH, 4-OH
Xe	4-OH

⇒ Top to bottom metallic character ↑ in M—OH bond ionic character ↑, no. of -OH holding capacity ↓

* $AsCl_3 \xrightarrow{Hydr.} As(OH)_3$

* $BiCl_3$, $SbCl_3$ $\xrightarrow{H_2O}$ complete hydrolysis not possible so, they show partial hydrolysis.

* $BiCl_3 \xrightarrow{H_2O} BiOCl + 2HCl$

Pearl ash
(Ionic comp)

* $SbCl_3 \xrightarrow{H_2O} SbOCl + 2HCl$

* $BiOCl \longrightarrow BiO^+ + Cl^-$

Bismuthyl Chloride
Bismuth oxychloride (Not a correct Name)

NCl_3 —Hydrolysis→ $NH_3 + HOCl$ ⟹ Slow S_N2

PCl_3 —"→ $H_3PO_3 + HCl$] complete S_N2

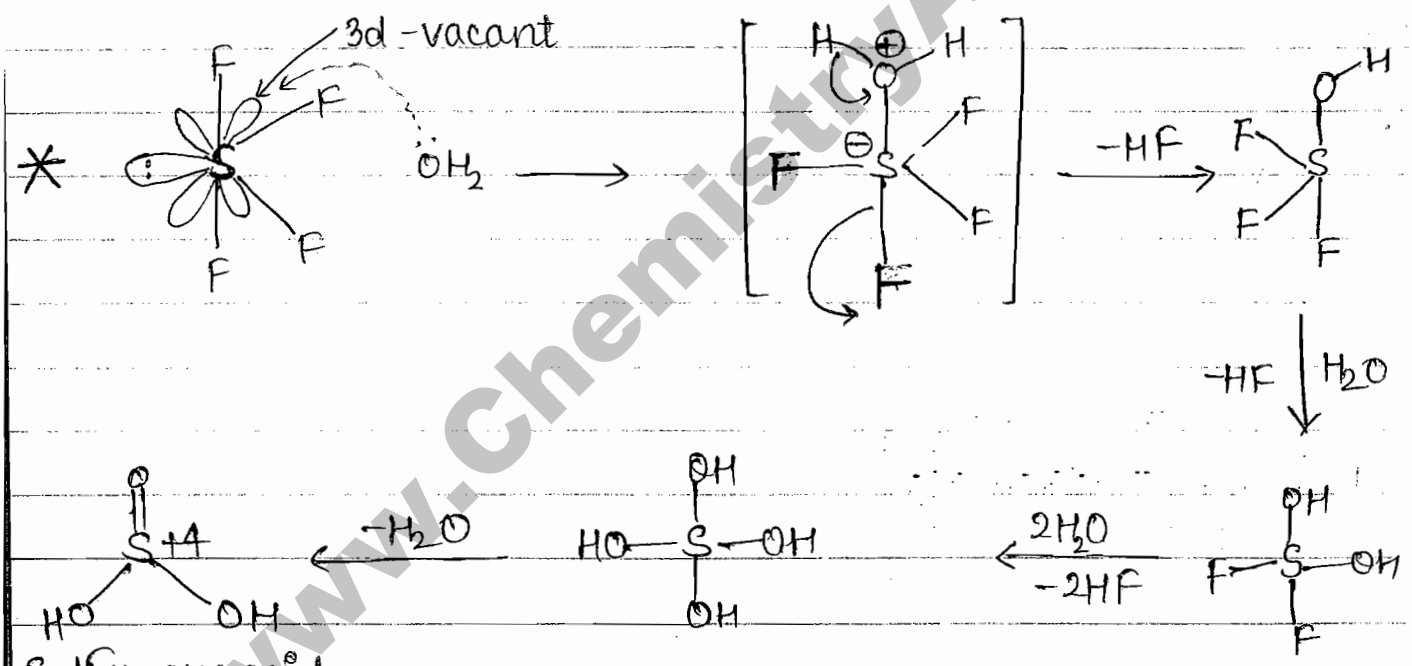
$AsCl_3$ —"→ $As(OH)_3 + HCl$]

$SbCl_3$ —"→ $SbOCl + HCl$] partial S_N2

$BiCl_3$ —"→ $BiOCl + HCl$]

S_N2 Hydrolysis order. $PCl_3 > AsCl_3 > NCl_3 > SbCl_3 > BiCl_3$

16-Group



Sulfurous acid.

* SF_4
SCl_4
SBr_4
SI_4

↓ S_N2 Rate ↓ because of Steric corwd ↑

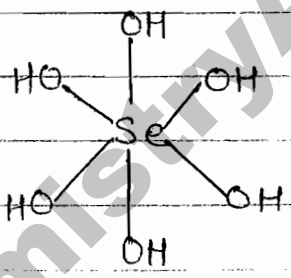
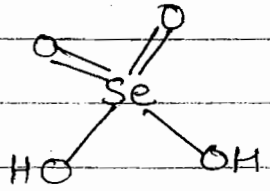
* SF_6 — Vacant d ✓, +ve charge on S ✓ | Although Hydrolysis of SF_6 via S_N2 not occurs because of very much steric crowding.

No Hydrolysis ⇒ Inert to Hydrolysis.

* SF_6 ← Inert no S_N2

SeF_6, TeF_6] slow S_N2

↳ More S_N2 Hydrolysis than SeF_6 because of big size of Te

* $SeF_6 \xrightarrow[-6\,HF]{6\,H_2O}$  $\xrightarrow{-2H_2O}$ 

Inert for Hydrolysis

* SF_6, SCl_6, SBr_6, SI_6 — S_N1 rate ↑

17th Group:-

Interhalogen Compounds:-

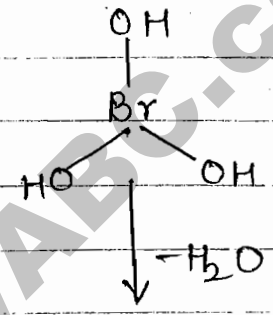
AB	AB_3	AB_5	AB_7
ICl	ICl_3	BrF_5	IF_7
BrF	BrF_3		

Hypochlorous $HOCl$
Chlorous acid $HClO_2$
Chloric " $HClO_3$
Per Chloric " $HClO_4$

* Central Atom should be big so 'F' never C. Atom.
* Surrounding atom " " small " I " surrounding atom

$\Rightarrow \overset{\delta+}{Cl}-\overset{\delta-}{F} + \overset{\delta+}{H}-\overset{\delta-}{OH} \longrightarrow HF + Cl-OH$

Hydra acid — Oxo acid

$\Rightarrow \overset{\delta+}{Br}\overset{\delta-}{F_3} \xrightarrow{\overset{\delta+}{3H}-\overset{\delta-}{OH}} 3HF +$ 

$\cdot\cdot Br-OH$ (or) $HBrO_2$
(or) $HBrO_2 \cdot H_2O$

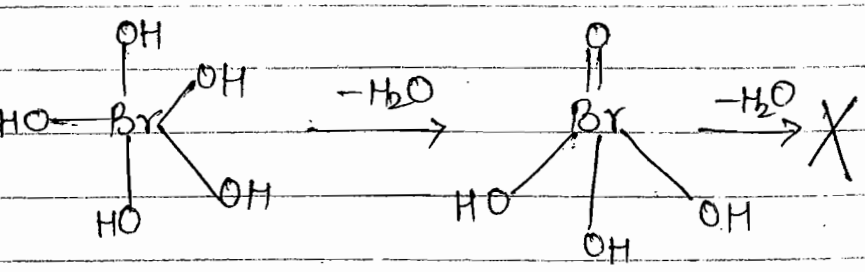
Q $\overset{+3}{Br}F_3 \xrightarrow{\text{Hydrolysis}} ?$

a) $HBrO$ b) $HBrO_3$ c) $H\overset{+3}{Br}O_2$ d) $HBrO_4$

$\Rightarrow$ Same oxidation state After Hydrolysis

Q $\overset{\oplus}{Br}F_3 \xrightarrow{Hyd.} ?$

a) $H\overset{+3}{Br}O_2$ b) $\overset{+3}{Br}(OH)_3$ c) $HBrO_4$ d) HBr

$\Rightarrow Br(F)_5 \xrightarrow[-5HF]{5H_2O}$ 

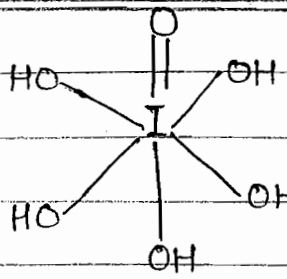
Further No hydrolysis

$Pb(OAc)_4$ (+4) $\xrightarrow{red^n.}$ Pb^{2+} ⇒ i.e. why $Pb(OAc)_4$ is oxidising agent.

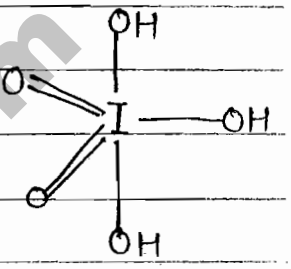
Unstable due to Inert pair

Stable.

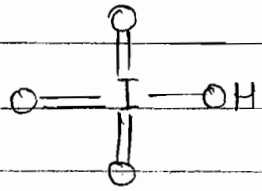
⇒ $IF_7 \xrightarrow[-7HF]{7H_2O} I(OH)_7 \xrightarrow{-H_2O}$



$\xrightarrow{-H_2O}$



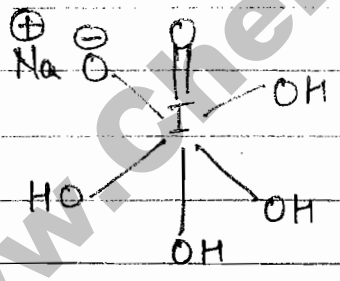
$\xleftarrow{-H_2O}$ $HIO_4 \cdot H_2O$ $\xleftarrow{}$



H_3IO_3

⇒ NaH_4IO_6 Malaparde Reagent used to oxidise diol, triols etc.

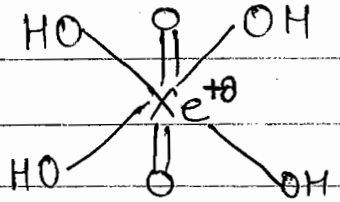
⇒ HIO_4 doesn't exist normally so it is not malaparde.



⇒ NaH_4IO_6

Hydrolysis of Xenon Flourides :-

The most stable hydroxide of Xe is H_4XeO_6



Tetrabasic Acid.

Champroportionation ⇒ $M^{\oplus}$ & $M^{\ominus}$ ⟶ becomes Neutral 2M.

Ex. $\overset{-3}{N}H_3 + H\overset{+3}{N}O_2 \longrightarrow N_2$

* $H_4\overset{+8}{X}eO_6$ (Perxenic acid) oxidising agent in Acid as well as basic medium. but exist in basic medium.
NET Ques.

* The stable oxide of Xenon are XeO_3 & XeO_2.
* XeO_3 used as explosive. (More than TNT.)
* If XeO_2 is formed in the reaction then it show disproportionation

⇒ $\overset{+4}{X}eO_2 \xrightarrow{\text{Disproportionation}} \overset{+6}{X}eO_3 + \overset{0}{X}e$

oxidn. ↑ XeO_2 → XeO_3; Redn. ↑ XeO_2 ← Xe^0

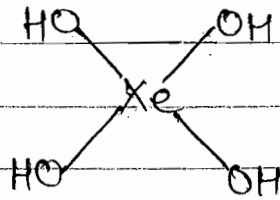
⇒ $Ag^{\oplus} + Ag^{\ominus} \longrightarrow Ag + Ag$ Camproportionation

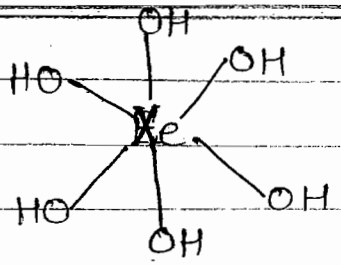
oxidn. ↓ $Ag^{\oplus}$ → Ag; Redn. ↑ Ag ← $Ag^{\ominus}$

GATE Ques.

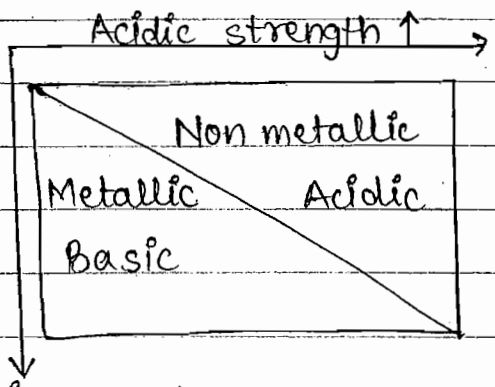
* If XeO formed then it convert into $Xe + \frac{1}{2}O_2$

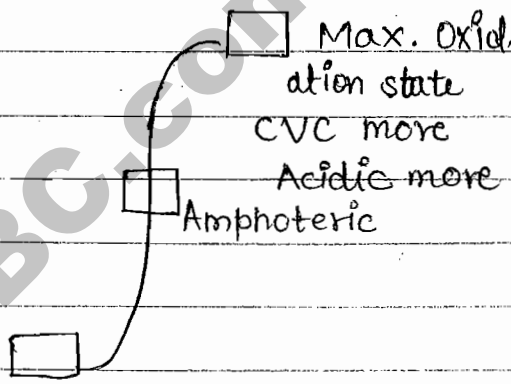
⇒ $XeF_2 \xrightarrow[-HF]{2H_2O} HO-Xe-OH \xrightarrow{-H_2O} Xe=O \downarrow Xe + \frac{1}{2}O_2$

⇒ $XeF_4 \xrightarrow[-4HF]{4H_2O}$  $\xrightarrow{-2H_2O} O=Xe=O \downarrow XeO_3 + Xe + \frac{1}{2}O_2$

$\Rightarrow \overset{+6}{XeF_6} \xrightarrow[-6HF]{6H_2O}$  $\xrightarrow{-3H_2O} \overset{+6}{XeO_3}$

Hydrolysis of Oxides:-





* $\overset{+4}{SO_2} < \overset{+6}{SO_3}$

Acidity ↑

* $\overset{+1}{N_2O} < \overset{+2}{NO} < \overset{+3}{N_2O_3} < \overset{+4}{NO_2} < \overset{+5}{N_2O_5}$

Acidity ↑

* $\overset{+1}{Cl_2O} < \overset{+3}{Cl_2O_3} < \overset{+4}{ClO_2} < \overset{+5}{Cl_2O_5} < \overset{+7}{Cl_2O_7}$

Acidity ↑

* $\overset{+2}{BeO} < \overset{+3}{Al_2O_3} < \overset{+4}{SiO_2} < \overset{+5}{P_2O_5} < \overset{+6}{SO_3} < \overset{+7}{Cl_2O_7}$

Acidity ↑

1 Molar solution of HCl is Buffer soln.

Potentia-de-hydrogenie ⇒ pH

10^5 ×

5 ← Powers always Bigger than Base

10 ← Base (Small)

* $\overset{+1}{Na_2O} < \overset{+1}{K_2O} < \overset{+1}{Rb_2O} < \overset{+1}{Cs_2O}$

Basicity ↑

The acidic and basic depends upon many factor –

1) Nature of solvent
2) Nature of comp. (% ionic & % covalent char).
3) Oxidation state
4)

⇒ for the comparision of oxide in which oxidation state of central atom max.

Acidic Strength ∝ Oxidn. State

⇒ For oxides of same elements with diff oxidation strength.

Acidic Strength ∝ Oxidn. State.

⇒ Oxides in which O.S. of C. Atom is intermediate (b/w max & min or near by zero), those oxides are usually Amphoteric. Ex. $\overset{+1}{N_2O}$ Neutral

⇒ Metal oxides are of two types –

i) Basic ii) ~~Neut~~ Amphoteric, Never Neutral.

⇒ Metals which are semimetal (or) metalloide oxide are amphoteric Ex.

$\underbrace{CO_2, SiO_2}_{\text{Non metal}}, \underbrace{GeO_2}_{\text{Metalloid}}, \underbrace{SnO_2 \quad PbO_2}_{\text{Metal (Almost metalloid)}}$

Acidic — Amphoteric

1M. HCl $pH = 0$

10M HCl pH = can't determine] GATE Ques.

PbO_2 (+4) + HCl → $[PbCl_4]$ (+4) Unstable → $PbCl_2$ (+2) Stable + Cl_2

PbO_2 (+4) + NaOH → $[Na_2PbO_3]$ (+4) Unstable → Na_2PbO_2 (+2) Stable + O_2

NET

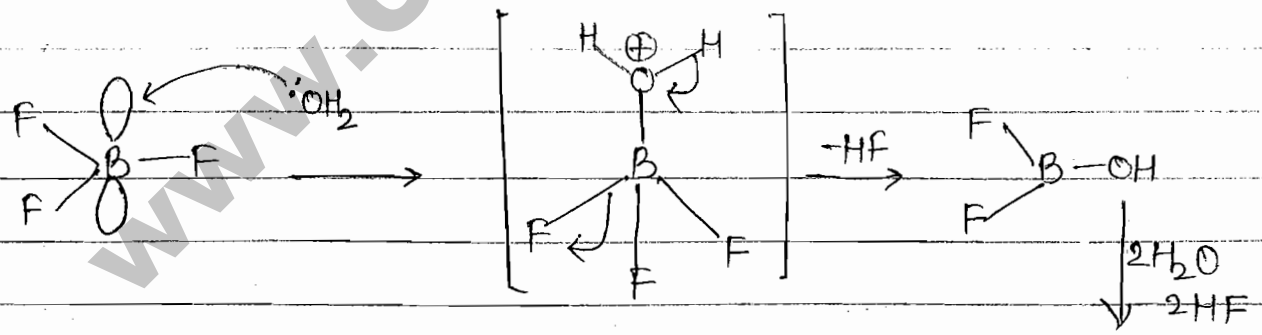
Q Acidic strength order ?

P_2O_5 (+5) < SO_3 (+6) < Cl_2O_7 (+7)

SO_2 (+4) < P_2O_5 (+5) < Cl_2O_7 (+7)

Hydrolysis of Boron Halides :-

BX_3 vacant 2p orb.



$B(OH)_3$

* BF_3 | Rate of hydrolysis ↑ because Bond length ↑

BCl_3

BBr_3

BI_3 ↓

Jorgegenson concept / Symbiosis :- Hard lig. have tendency to attack at those places which already have such type of Hard lig.

$BF_3 \xrightarrow{H^{\ominus}} X$; $BF_3 \xrightarrow{F^{\ominus}} BF_4^-$

$BH_3 \xrightarrow{H^-} BH_4^-$; $BH_3 \xrightarrow{F^-} X$

Q Hydrolysis of BF_3 in Basic medium, prod ?

$$BF_3 \xrightarrow{H_2O} B(OH)_3 \xrightarrow{Base} [B(OH)_4]^{\ominus}$$

Q Hydrolysis of BF conc. prod?

$$\underbrace{BF + H_2O}_{\text{conc. means } H_2O \text{ molecule very less.}} \longrightarrow F_2B-OH + HF$$

$F_2B-OH \longrightarrow H^{\oplus}[BF_3OH]^{\ominus}$

No further hydrolysis becoz. of H_2O very less.

Q How many moles of H_2O are required for hydrolysis of 1 mole of SiF_4 ?

$$SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HF$$

$$2SiF_4 + 4HF \longrightarrow 2[H_2[SiF_6]]$$

Net Rxn. $3SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + 2H_2[SiF_6]$

Ans. 4/3

Hydrolysis of Element :-

Metals on Rxn. with water ~~called~~ form Hydroxide.

Ex.

$$Na + H_2O \longrightarrow NaOH + H_2\uparrow$$

Non metals on
In the rxn. is carried in less amount of H_2O oxo acids of intermediate

Ex.

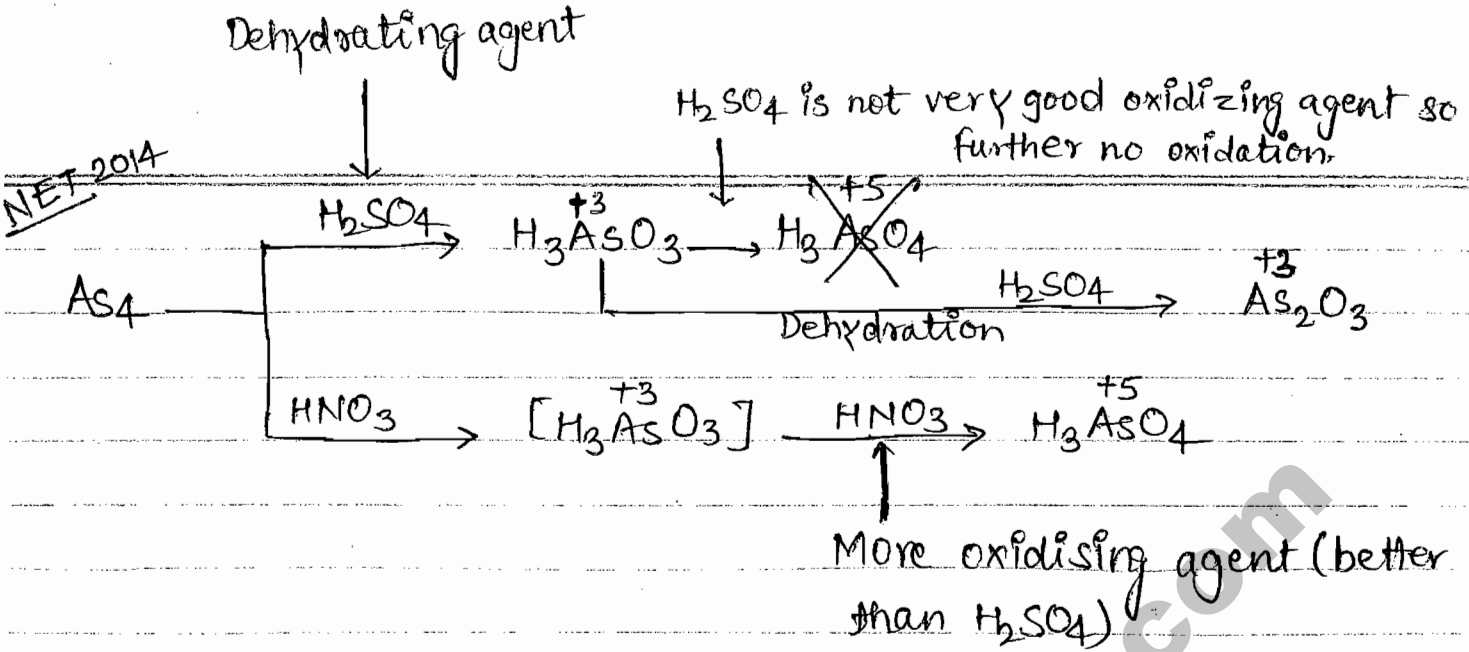
P_4 —
- H_2O limited → $H_3\overset{+3}{P}O_3$ orthophosphoric acid.
- H_2O excess → $H_3\overset{+5}{P}O_4$ " " "

S_8 —
- H_2O limited → $H_2\overset{+4}{S}O_4$ " Sulphuric "
- H_2O excess → H_2SO_4 " " "

Oxidizing agent like HNO_3, H_2SO_4, can do above rxn.

NET. 2014

P_4 —
- H_2SO_4 → $[H_3PO_4]$ $\xrightarrow{H_2SO_4}$ P_2O_5 (→ Water abstraction)
- HNO_3 → H_3PO_4



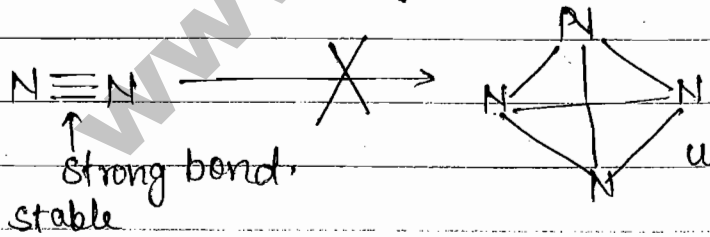
In As some inert pair effect that is why H_2SO_4 unable to oxidise it upto +5 O.S. while P do not so Inert pair effect i.e why H_2SO_4 oxidise it upto +5 O.S.

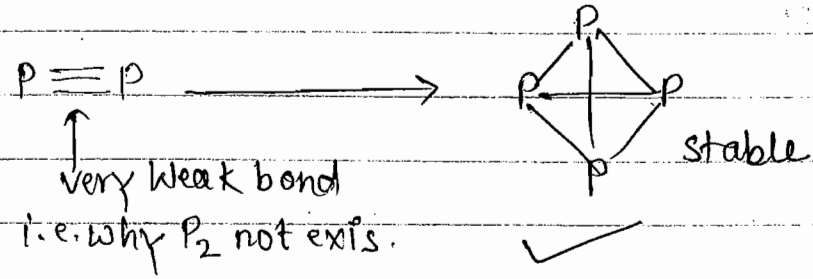
NITROGEN FAMILY

Group 15.

Pincogenes ⇒ suffocation family. $ns^2\ np^3$

* Nitrogen is diatomic gas, while P, As, Sb are tetra atomic solid & Bi is metallic
* N_2 → Behave as very poor lewis base.





NET

Bond Energy:- $C-C > N-N > O-O > F-F$ (strongest bond: C—C; weakest bond: F—F)

size ↓ i.e. why l.p.-l.p. repulsion.

* $N-F < P-F > As-F < As-F$

Small size — less N—F bond length so more l.p.-l.p. resulsion — Weakest bond

Big size — Large bond less l.p.-l.p. repulsion.

* $N-H > P-H > As-H$

Oxidation state

$-3, +3, +5$

Maximum no. of O.S. shown in this group

N = −3 to +5

Ex. NH_3 (−3), N_2H_4 (−2), NH_2OH (−1), N_2 (0), N_2O (+1), NO (+2), N_2O_3 (+3), NO_2 (+4), N_2O_5 (+5)

Allotropy:-

Max. shown by P,-

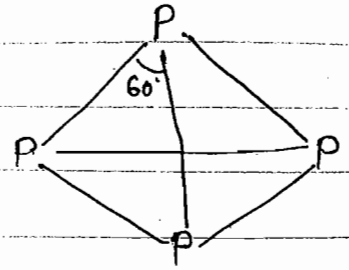
White P, Red P, Black P, Scaletet P, Violet P. etc.

$$Ca_3(PO_4)_2 + SiO_2 \longrightarrow CaSiO_3 + P_4O_{10} \xrightarrow{\Delta\ C}$$

$\longrightarrow [CO_{(g)}\uparrow + P_{4(g)}\uparrow] \xrightarrow{\text{cooling}} P_4 \xrightarrow[\text{\& Press}]{\text{high temp}} P_4\,(\text{Black})$

$P_4 \xrightarrow{\Delta \text{ or } h\nu} \text{Red } P_4$

White 'P' :-



Total 60° Angle = 12
Faces = 4

Drago Rule ⇒ 'No Hybridization at elemental state

If ques. asked then most appropriate hyb. ⇒ sp^3

P% = 75%

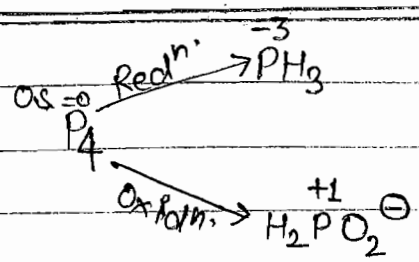
Normal sp^3 ∠θ = 109°28'
in P_4 ∠θ = 60° (Highly strained)

⇓

Due to strain P_4 is highly Reactive.

White P_4 is the most reactive allotrop of 'P' because of:
1) Angle strain
2) Increased 'p' character & bond length
⇒ Only white P_4 is soluble in CS_2, Benzene, CCl_4 & it is the only 'P' form which react with alkali and undergo disproportionation.

$P_4 + NaOH \longrightarrow PH_3 + Na.H_2PO_2$
white — Phosphine — Sod. Hypo phosphite



Equivalent wt. in Redox

$$E = \frac{\text{Mol. wt}}{Z}$$

Z ↑ change in O.S.

Ex. $K_2Cr_2O_7 \xrightarrow{H^{\oplus}} Cr^{3+}$

$+2+2x-14=0$ $\quad$ $Cr = +3$

$2x = 12$ $\quad$ $2Cr = +6$

change (Z) = 6

$$E = \frac{\text{M. wt}}{6}$$

Ex. $KO_3 \longrightarrow K_2O$

$+1+3x=0$ $\quad$ $1\text{'O'} = -2$

$3x = -1$ $\quad$ $3\text{'O'} = -6$

$Z = 5$

$$E = \frac{M}{5}$$

Ex.

$KMnO_4$ oxidising agent in all medium

~~ad~~ acidic	M/5	pH ↑
Neutral	M/3	
Basic	M/1	

a) Acidic

$KMnO_4 \xrightarrow{H^{\oplus}} Mn^{2+}$

1 Mn = +7 → 1 Mn = +2 ; M/5

z = 5

b) Neutral

$KMnO_4 \xrightarrow{H_2O} MnO_2$

1 Mn = +7 → 1 Mn = +4 ; M/3

z = +3

c) Alkaline $KMnO_4 \longrightarrow K_2MnO_4$

1 Mn = +7 → 1 Mn = +6

z = 1

Firstly K_2MnO_4 is formed & after some time it changes in MnO_2

Oxidation :-

$\overset{+3}{C_2O_4}^{--} \longrightarrow \overset{+4}{CO_2}$

$\overset{+4}{CO_3}^{--} \longrightarrow$ No Rxn. because C is highest O.S. (+4)

$\overset{4-}{AsO_3} \longrightarrow \overset{+5}{AsO_4}^{---}$

$Fe^{++} \longrightarrow Fe^{3+}$

$H_2\overset{-2}{S} \longrightarrow \overset{0}{S} \longrightarrow \overset{+6}{S}O_4^{2-}$

$I^{\ominus}/HI \longrightarrow I_2$

$Cl^{\ominus}/HCl \longrightarrow Cl_2$

$Br^{\ominus}/HBr \longrightarrow Br_2$

Ferrocynide $\longrightarrow$ Ferricyanide

$S \longrightarrow SO_4^{2-}$

* $\overset{-3}{N}H_3 \longrightarrow N_2 + H_2$

$\overset{-3}{N}H_3 \xrightarrow{\text{oxidn}} \overset{0}{N}_2$

$N = -3 \qquad 1N = 0$

$n_1 = 3$

$\overset{+1}{N}H_3 \xrightarrow{\text{Redn.}} H_2$

$1H = +1 \qquad 1H = 0$

$3H = +3 \longrightarrow 3H = 0$

$n_2 = 3$

$$E = \frac{M}{n_1} + \frac{M}{n_2} = \frac{M}{6}$$

* $FeC_2O_4 \xrightarrow[\text{oxidn.}]{KMnO_4/H^{\oplus}}$

$Fe^{2+} \longrightarrow Fe^{3+}$

$Z_1 = 1$

$C_2O_4^{2-} \xrightarrow{\text{oxidn.}} CO_2$

$2C = +6 \xleftrightarrow{Z_2 = 2} 2C = +8$

$E = \frac{M}{Z_1 + Z_2} = \frac{M}{3}$

* $P_4 \xrightarrow{NaOH} PH_3 + NaH_2PO_2$

$P_4 \xrightarrow{\text{Redn}} PH_3$ · $1P = -3$

$4P = 0$ $\qquad$ $4P = -12$

$Z = 12$

$P_4 \xrightarrow{\text{Oxidn.}} H_2PO_2^-$

$4P = 0$ $\qquad$ $1P = +1$

$4P = +4$

$Z = 4$

$E = \frac{M}{12} + \frac{M}{4} \Rightarrow \frac{4M}{12}$

* $Cu_2S \xrightarrow[KMnO_4/H^{\oplus}]{Oxidn.}$

$1Cu^{+} = +1 \xrightarrow{Oxidn.} Cu^{++}$

$2Cu^{+} = +2 \qquad 2Cu = +4$

$Z_1 = 2$

$S^{2-} \xrightarrow{Oxidn.} SO_4^{2-}$

$1S = -2 \qquad 1S = +6$

$Z_2 = 8$

$E = \frac{M}{Z_1 + Z_2} = \frac{M}{10}$

* $HCHO \xrightarrow{\overset{\ominus}{OH}} CH_3OH + HCOO^{\ominus}$

$1C = 0 \qquad 1C = +2 \qquad 1C = -2$

Oxidn. $Z = 2$

Redn. $Z = 2$

$E = \frac{M}{2} + \frac{M}{2}$

NET/GATE

Most imp

Q $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + I^{\ominus}$

Sod. thiosulphate — Sod. tetra thionate

$2 + 2x - 6 = 0$

$2x = 4$

$x = 1$

$+2 + 4x - 12 = 0$

$4x = 10$

$2x = 5$

$$E = \frac{M.wt}{1}$$

Equivalent wt.

Simple

Q $Na_2S_2O_3 \longrightarrow Na_2S_4O_6$ Eq. wt. ?

$2S = +4$

$4S = +8$

$4S = 10$

$z = 2$

Eq. wt. of $Na_2S_4O_6$

$$E = \frac{M.wt}{2}$$

Simple

Q $Br_2 + {}^{\ominus}OH \longrightarrow Br^{\ominus} + BrO_3^{\ominus}$

$E = ?$

$2Br = 0$

$1Br = -1$

$1Br = +5$

$2Br = 0$

$2Br = -2$

$2Br = 10$

$z_1 = 2$

$z_2 = 10$

$$E = \frac{M}{z_1} + \frac{M}{z_2}$$

$$E = \frac{6M}{10}$$

Q $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$

1P = +3 → 1P = −3 (z = 6); 1P = +3 → 1P = 5 (z = 2)

$$E = \frac{M}{6} + \frac{M}{2} = \frac{2M + M}{12}$$

Eq. wt of salt.

* NaCl

$$E = \frac{M}{1} \leftarrow \text{charge.}$$

* Na_2SO_4 $E = \frac{M}{2}$

* $Fe_2(SO_4)_3$ $E = \frac{M}{6}$

* $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Alum.

$E = \frac{M}{8}$ In all the alum devide M. wt by 8

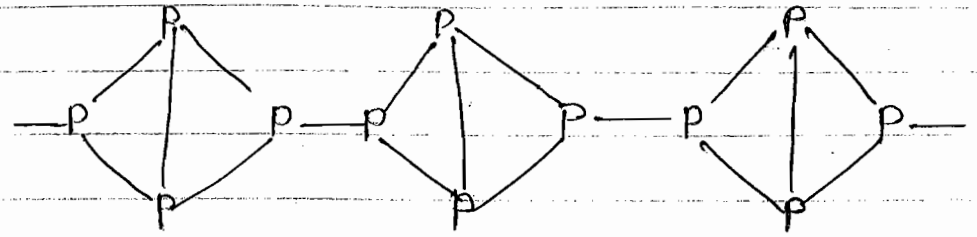
* Mohr Salt $FeSO_4(NH_4)_2 \cdot SO_4 \cdot 6H_2O$

$$E = \frac{M}{4}$$

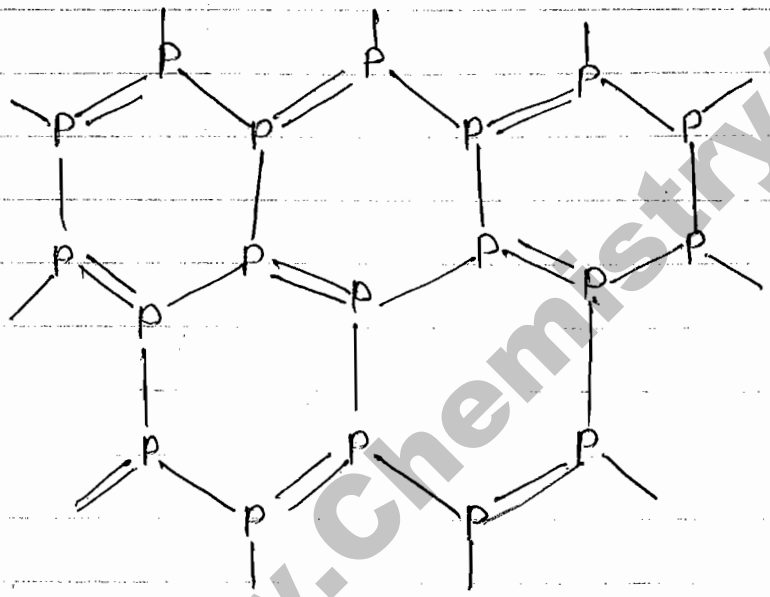
भूत की लालटेन ⇒ Phosphorous

Disease by white 'P' ⇒ "Phoosy Jaw"

Red Phosphorus chain form.



Black 'P' Similar to Graphite



Most stable alloy of 'P' is black phosphorous.

* Home signals ($CaC_2 + Ca_3P_2$)

* White 'P' ⇒ Softest form (Alloy) of 'P'.

* No yellow 'P', it's white 'P' on reacting oxide becomes yellow.

* Passivity :- Formation the oxide layer over the surface of metal is called passivity. due to this the inner layers get protected. Hence Al is used in

making aeroplanes, HNO_3 transported in Al vessels.
Coating of Pt is called ~~Shiramoyedi~~ Sheramidising.

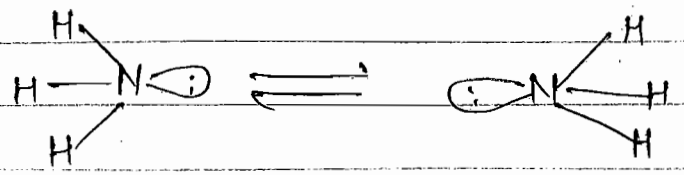
Hydrogen Compounds:-

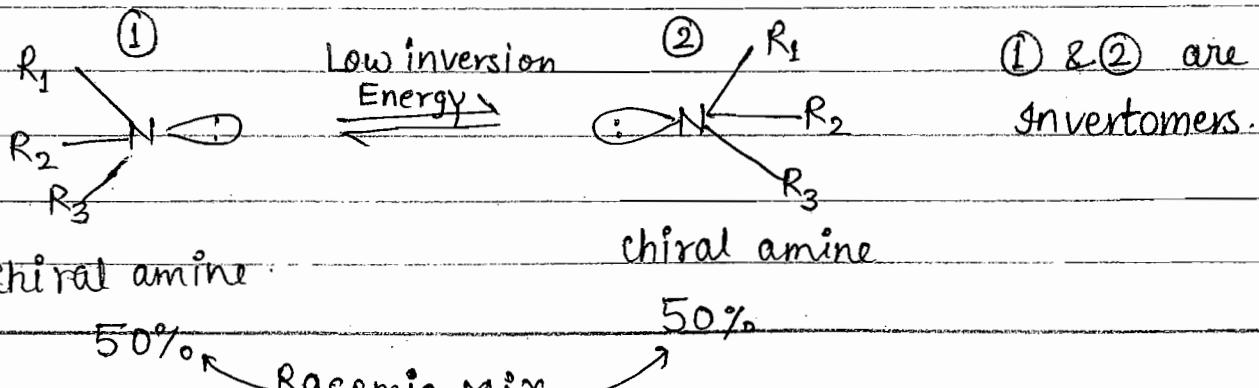
NH_3	Δ_0 ↓
PH_3	Hyb. ability ↓
AsH_3	Basicity ↓
SbH_3	T.S. ↓
BiH_3	↓

	IUPAC Name
NH_3	Azane
PH_3	Phosphane
AsH_3	Arsane
SbH_3	Stibane
BiH_3	Bismuthane

Umbrella Inversion.

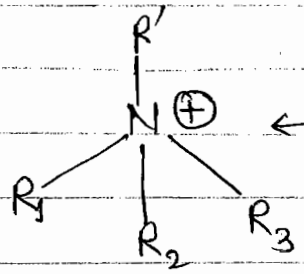
(a) Amine inversion



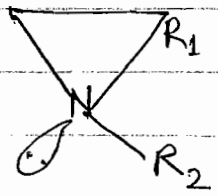


Inversion Energy ∴ $PR_3 > AsR_3 > SbR_3 > NR_3$

due to high inversion Energy no inversion at low temp., hence these compound can be resolve.



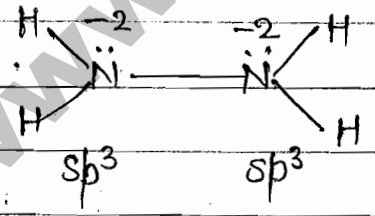
← No inversion, can be resolve.



Aziridene

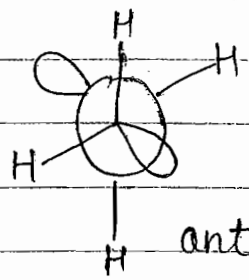
Hydrazine

$$NaOCl + NH_3 \longrightarrow NaCl + N_2H_4 + H_2O$$

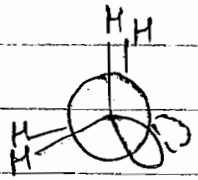
N_2H_4 

sp^3 sp^3

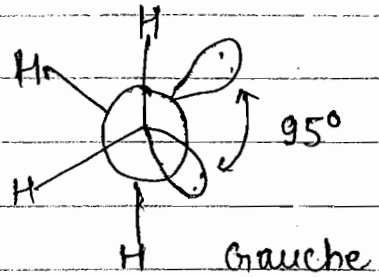
⇒ Many conformers.



anti

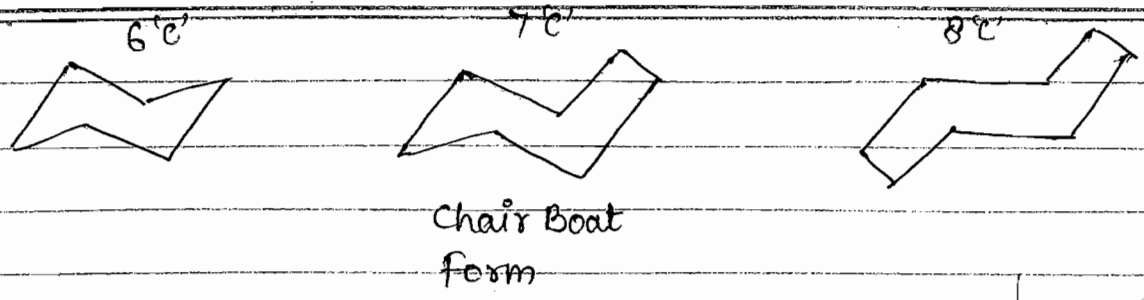


Eclipsed.



Gauche

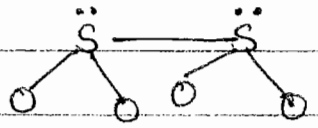
Most stable



Chair Boat form

In hydrazine, due to electronegativity factor and due. angle 95° gauche form (@ semi gauche) is more stable & Hydrazine forms four 'H'-bond.

⇒ $S_2O_4^{2-}$



Eclipsed form more stable due to symmetric str. l.p.-l.p. repulsion less due to big size of 'S'

⇒ CH_3-CH_3 ⇒ Anti more stable.

⇒ GeH_3-GeH_3 ⇒ Eclipsed because 'Ge' big size no repulsion.

16/10/2014

group.

Polyphospho Nitrilic Halides (or) Phosphazenes.

General formula. $\left[N=\underset{\underset{X}{|}}{\overset{X}{\overset{|}{P}}}-\right]_n$ discovered by Wohler

X = Cl, Br, F, OMe, Ph etc. n = 3-7

GATE

Preparation

$$NH_3 + PCl_5 \longrightarrow (NPCl_2)_3 + HCl$$

$$NH_3 + PCl_5 \longrightarrow (NPCl)_4 + HCl$$

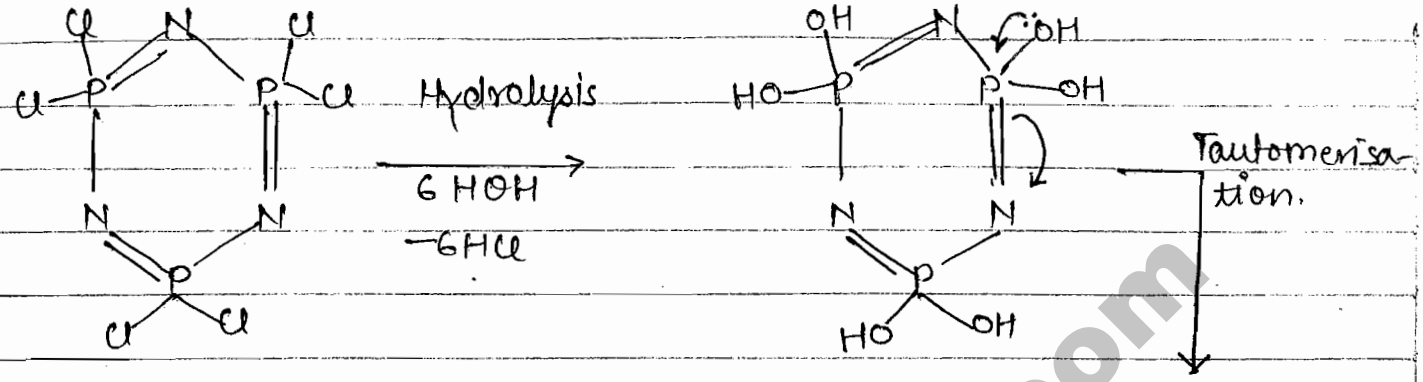
Modern method:-

$$PCl_5 + NH_4Cl \xrightarrow[C_6H_5Br \text{ (or)}]{C_2H_4Cl_2 \text{ (or)}}_{140-150^\circ C} (NPCl_2)_n + HCl$$

Reactions

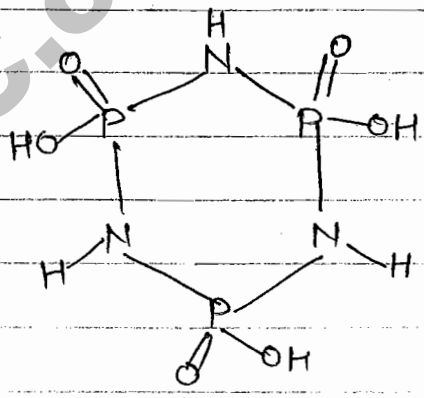
$(NPCl_2)_3$ reacts with:

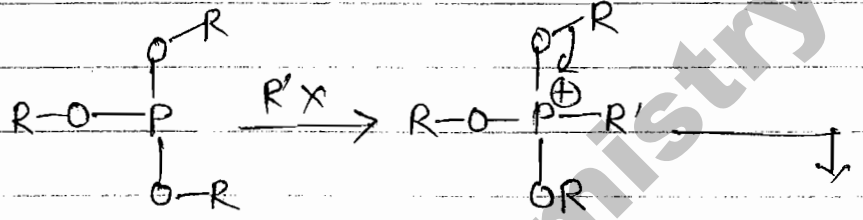
- $6NaF$, $-6NaCl$ → $(NPF_2)_3$
- $6KSO_2F$, $-6KCl$, $-6SO_2$ → $(NPF_2)_3$
- $6NaOMe$, $-6NaCl$ → $[NP(OMe)_2]_3$
- $6NaOEt$, $-6NaCl$ → $[NP(OEt_2)]_3$

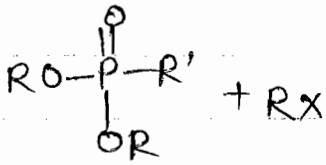


NET

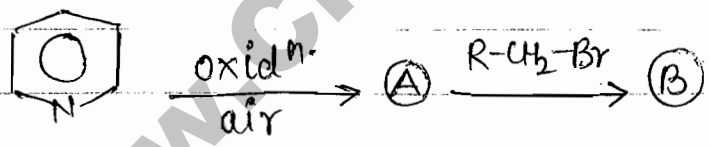
* Phosphorus has very high tendency to tautomerisation.

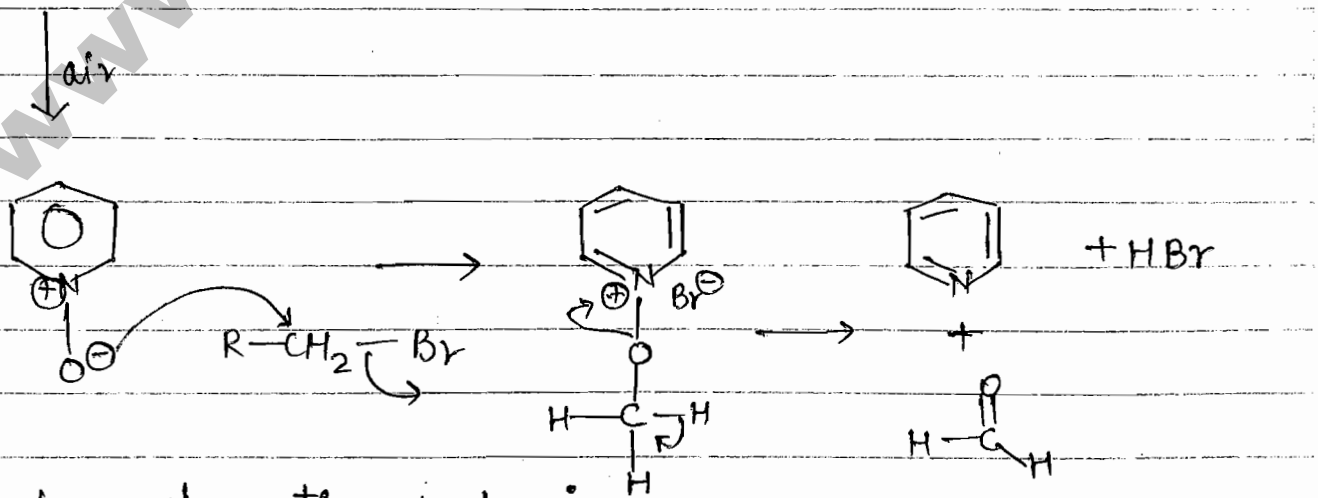






2007
NET

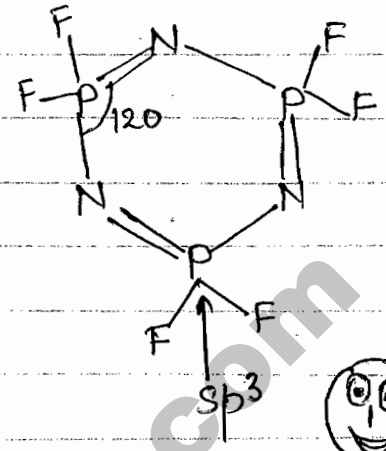




Hezenberg - dementis pulmari reaction

Structure

$[NPF_2]_3$ ⇒ Planar

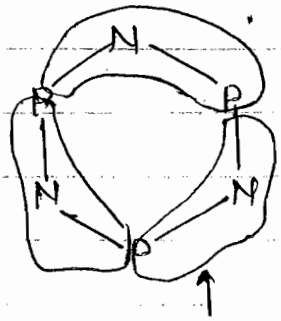


$[NPCl_2]_3$ ⇒ Nearly planar

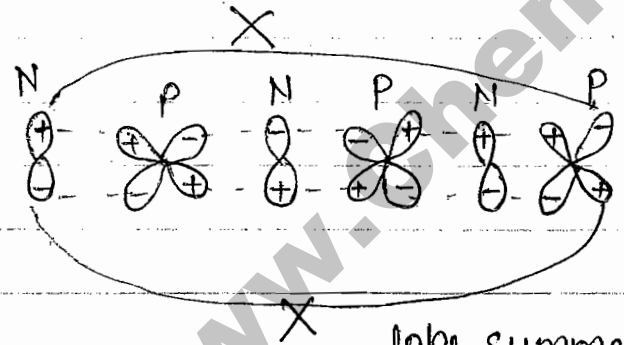
N = [1L] [1|1|1] (sp2, 2pz)

P = [1] [1|1|1], [1] (Sp3, 3d)

3 Island Bonding ⇒



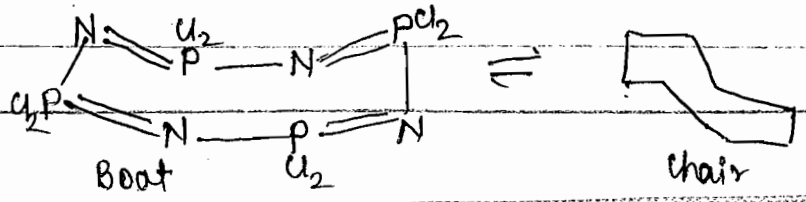
Island bonding
(Not complete π delocalisation)

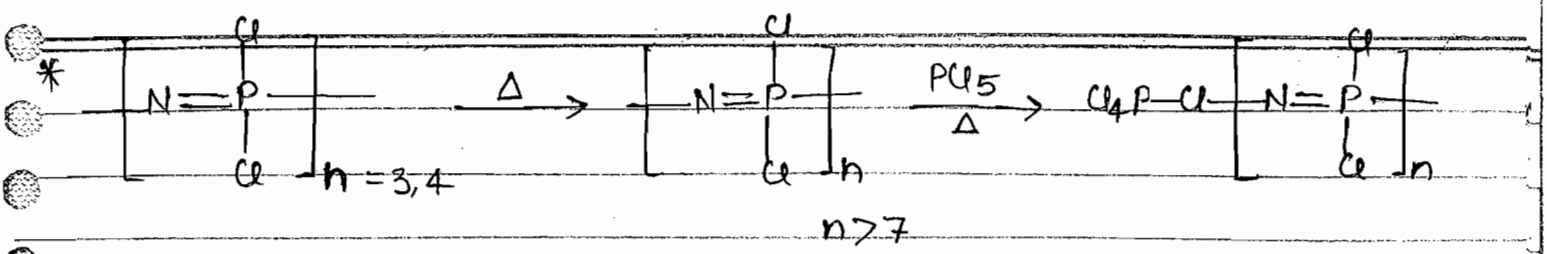


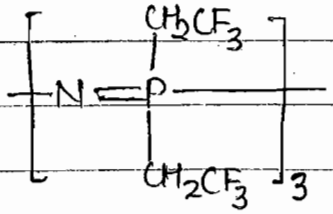
lobe symmetry not matching.
so no complete π delocalization

In $[NPCl_2]_3$ no perfect bonding model has been given so for. on the basis of X-Ray studies concepts of Island bonding. ∴

$[NPCl_2]_4$ ⇒ It has 8 memb. puckered ring str.



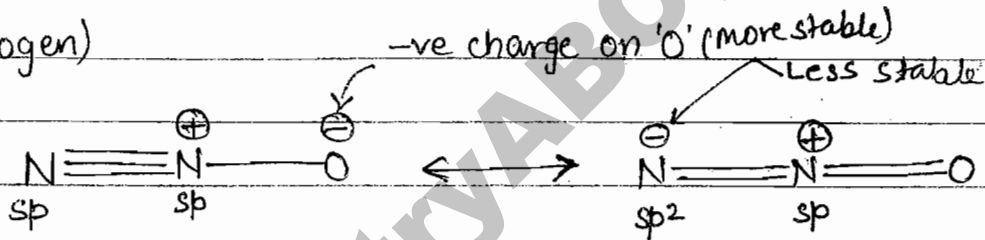




Highly resistant for H_2O
used in making artificial blood vessels, pace maker.

Oxides :- (Nitrogen)

N_2O :- Laughing Gas

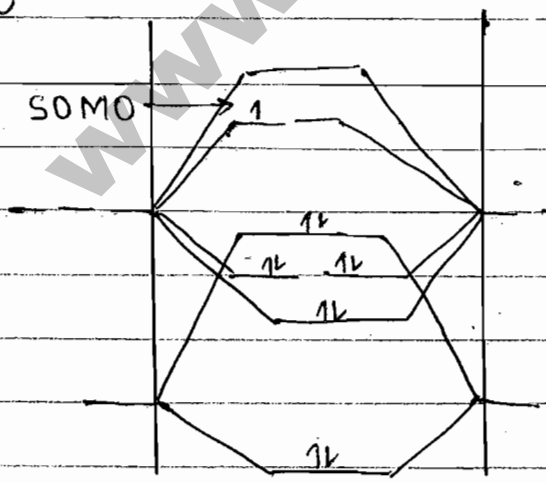


I ⟷ II

Stability ⇒ I > II

N_2O is used in whipping creams because veg oil easily mix.

NO



NO ⇒ 1 or 3 e^- donor

B.O = 2.5 (NO)

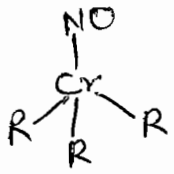
B.O = 3 (NO^+)

Ring Test of Nitrate

NO_3^- $\xrightarrow[FeSO_4]{\text{con. } H_2SO_4}$ Brown-violet ring ↓

$[Fe(H_2O)_5NO]SO_4$ ← $[Fe(SO_4)NO]$

Nitroso ferrous sulphate.



Low spin even Td.

R = $SiMe_3$

In 1979 Chen & Jolly reported with the help of Mossbauer that the str. $[Fe(H_2O)_5NO]^{++}SO_4^{-}$ is incorrect. Actual str. is $Fe^{2+}{=}NO$

(+1 and +1)

The decreament in μ from 5.1 BM to 3.9 BM clearly indicate it ($Fe^{2+}{=}NO$) existance.

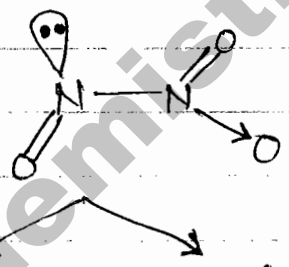
↑ covalent bonding (Not NO transffered totally e^-)

$\overset{+3}{N_2O_3}$

* NO is the free radical, it is the booster of gasolin along with N_2O.
* NO is involved in cell signaling (used in heart disease)

Most Imp.

Dinitrogen trioxide.

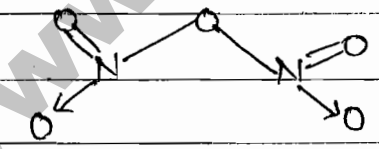


$(NO)_2 \leftrightharpoons \dot{N}O$ $\qquad$ $\dot{N}O_2 \rightleftharpoons N_2O_4$

$\dot{N}O_2$ don't dimerise due to bigger size & e^- is in high energy & in bigger orbital

N_2O_5

Solid



$\overset{+1}{N_2O}$ $\qquad$ $\overset{+2}{NO}$ $\qquad$ $\overset{+3}{N_2O_3}$ $\qquad$ $\overset{+4}{NO_2}$ $\qquad$ $\overset{+5}{N_2O_5}$

$\downarrow H_2O$ $\qquad$ $\downarrow$ $\qquad$ $\downarrow H_2O$ $\qquad$ Mixed oxide $\qquad$ $\downarrow H_2O$

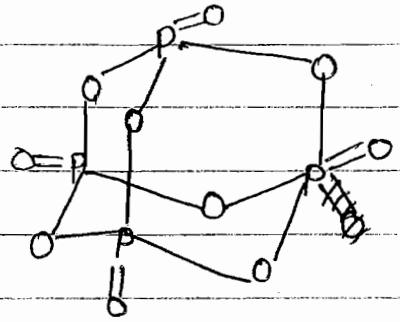
OXO acids: $H_2N_2O_2$ $\qquad$ HNO_2 $\qquad$ $\overset{+3}{HNO_2} + \overset{+5}{HNO_3}$ $\qquad$ $\overset{+5}{HNO_3}$

Oxides of 'P' :- Usually exist in dimeric form.

1) $\overset{+3}{P_2O_3} \equiv (P_2O_3)_2 \equiv P_4O_6$ Phosphorous trioxide

2) $\overset{+5}{P_2O_5} \equiv (P_2O_5)_2 \equiv P_4O_{10}$ Phosphorous penta oxide

3) P_4O_{10} ⇒ Admantane like str.



POP bonds = 6
P=O bonds = 4
rings = 3

* As_4O_6 similar to P_4O_6
* As_4O_{10} " " P_4O_{10}

N_2O	+1	
NO	+2	O.S. ↑
N_2O_3	+3	Acidic
NO_2	+4	strength ↑
N_2O_5	+5	↓

N_2O_5	Acidic
P_2O_5	Strength ↓
As_2O_5	↓

Sulphur Nitride @ Thiazines compound.

gmp S_4N_4 Tetra sulphur tetra Nitride.

Preparation :-

$$S_2Cl_2 + NH_3 \longrightarrow S_4N_4 + HCl$$

$$S + NH_3 \longrightarrow S_4N_4 + H_2 \text{ or } H_2S$$

$$S + NH_4Cl \longrightarrow S_4N_4 + HCl$$

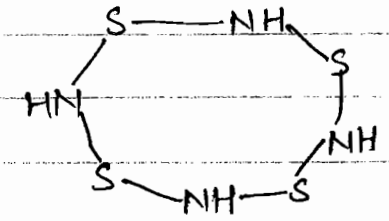
Acidity ⇒ CH_3COOH > CH_3COOOH

acid. — Per acid.

conjugate Base more stable — conj. Base less stable

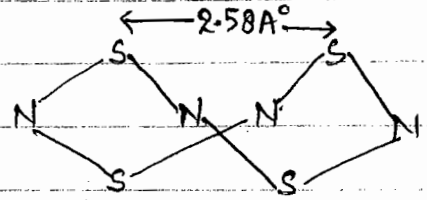
Per acids are always weaker than their acids.

Properties:- $S_4N_4 \xrightarrow{BF_3} S_4N_4^+ \cdot BF_4^-$

$S_4N_4 \xrightarrow[MeOH]{SnCl_2}$ 

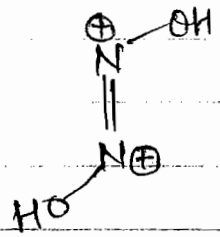
$S_4N_4 \xrightarrow[Imp.]{\Delta} (SN)_x$ Poly thiazyl

Super conductor at 0.23 K

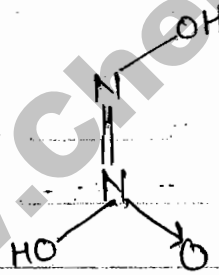
Structure:- 

Cradle shaped.

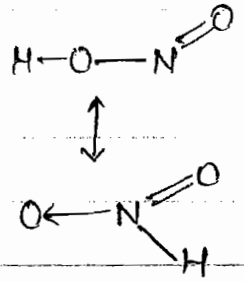
Oxo acids of 'N'



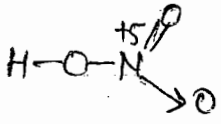
Hypo nitrous acid



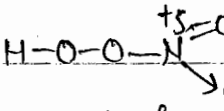
hyponitric acid



Nitrous acid



Nitric acid



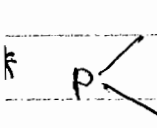
per Nitric acid

Imp.

Oxo acids of 'P' :-

'P' always penta valent

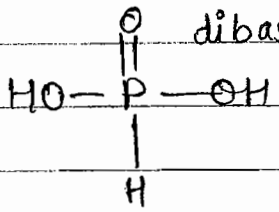
'P' Minimum str. $-\overset{OH}{\underset{|}{P}}=O$



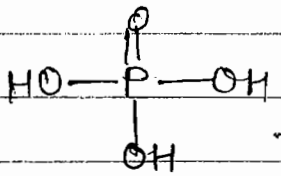
* -OH Responsible for acidic Nature
* P-H " " Reducing "
* P ⇒ sp^3 hyb.

M. I. P.

Ortho:- Max. O.S. of Parent series. → Orthophosphorous acid (+3) H_3PO_3 ; Orthophosphoric acid (+5) H_3PO_4



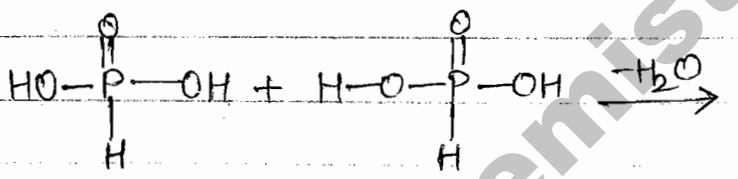
P—H Bond ⇒ Reducing agent

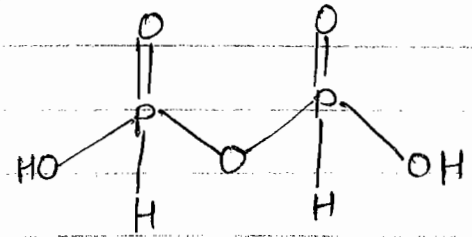


Tribasic acid

Not a reducing agent.

Poly oxo acids:- Product obtained by removing $n H_2O$ from (n+1) Parent acids.





Pyro phosphorous acid.

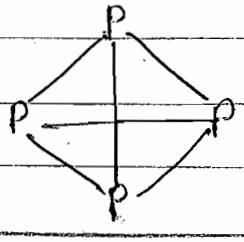
Hypo oxo acids:- Changed O.S. than +3 or +5 (formed by incomplete hydrolysis)

Meta oxo acids:- $-n H_2O$ forming circle or linear chain polymers.

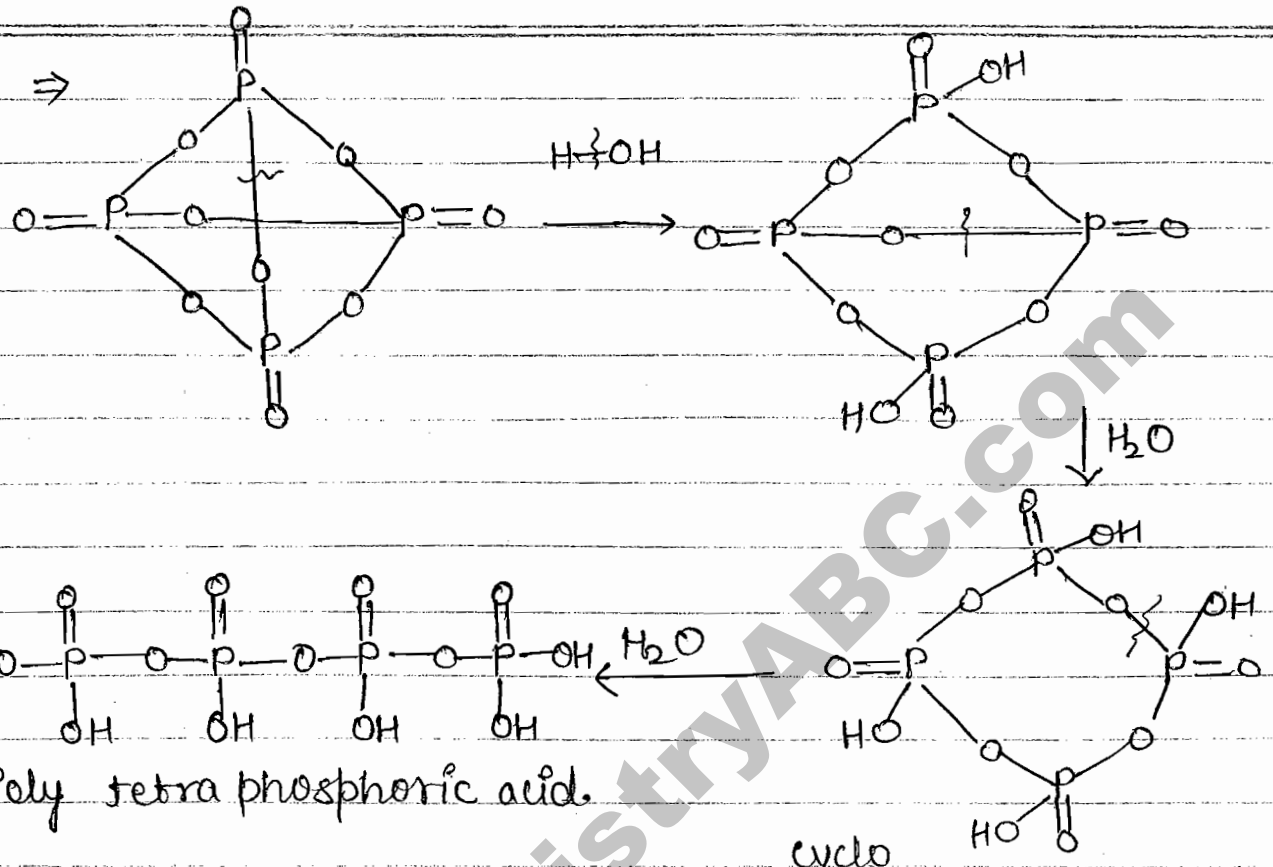
Pyro oxo acids:- $-1 H_2O$ from two parent acids of same series.

⇒ $P_4O_{10} + H_2O$ —?

P_4 str. ⇒



P_4O_{10} ⇒



Poly tetra phosphoric acid.

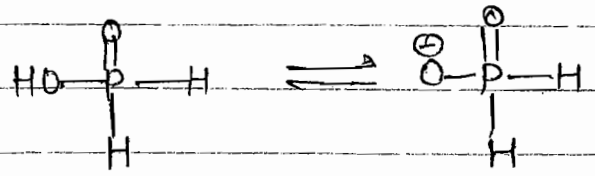
cyclo tetra phosphoric acid.

Q How many moles of H_2O are needed to convert one mole of P_2O_5 into poly tetraphosphoric acid?

Q How many moles of H_3PO_4 are formed by complete hydrolysis of one mole of phosphoric anhydride.

Oxo Hypo, acids: $H_3\overset{+1}{P}O_2$, $H_2\overset{+4}{P}O_3$

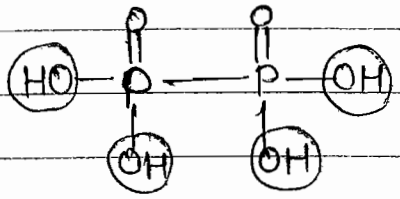
H_3PO_2 n=1 (Hypophosphorous acid)



conj Base

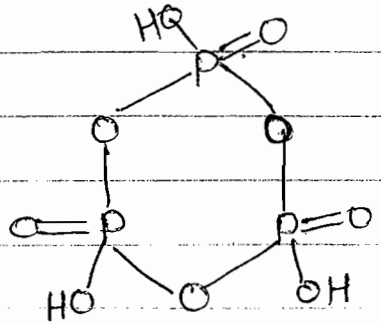
$C_6H_5-N_2Cl + (H_3PO_2 + H_2O) \longrightarrow C_6H_6 + N_2 + HCl + H_3PO_3$

Q Basicity of H_3PO_3 (acid) ⟹ This exists in dimeric form.

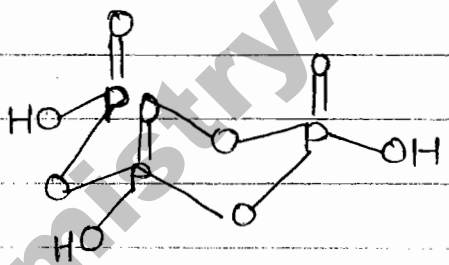


tetra basic acid.
but in formula (H_3PO_3) there are not 4 OH seems so don't confuse.

Meta oxo acids:- exist in salt form generally cyclic



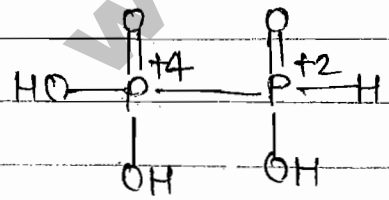
⟹



^{31}P **NMR**
1 Signal which is splitted into Triplet.

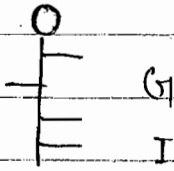
Due to big size of (P) ⇒ No Hydrogen bonding so OH equatorial.

IUPAC Notation.



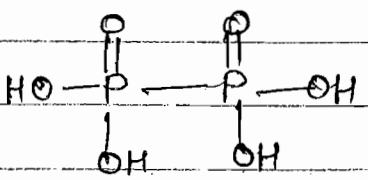
(a)

$[P^4-P^2]$ acid.
IUPAC Notation.

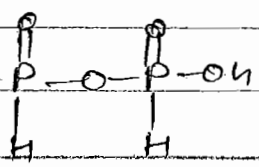


Glucose
IUPAC Notation

$[P^4-P^4]$ ⇒



$[P^4-O-P^4]$ ⇒



~~Chapter~~ - 16-Group.

CHALCOGENs ⇒ Ore forming family

Oxygen Family.

Don't use inert pair effect for this family

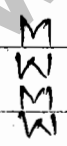
O
S
Se
Te
Po

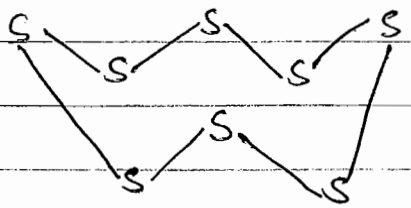
In 16 group don't consider IPE. but size factor should consider, As the size of central atom of surrounding atom increases, generally T.S. ↓.

Allotropy of Sulfur: α-sulfur (or) S Rhombic
β-sulfur (or) S monoclinic
γ-sulfur
Plastic sulfur, colloidal S etc.

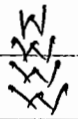
In the common form of S i.e. α, β it exist in octaatomic form. ~~common form of S~~ it S_8 unit the S_8 unit have puckered like str.

S_x ⇒





S_β =

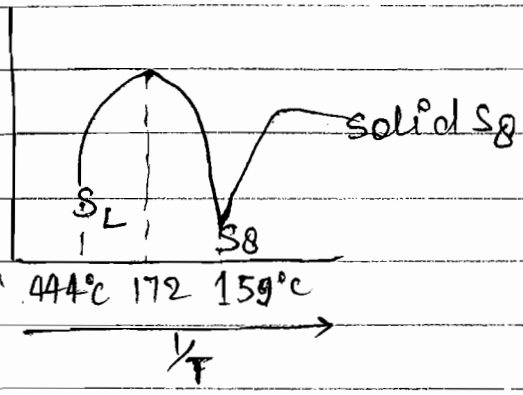


The viscocity curve of S is not regular, on increasing the temp. Viscocity firstly decreases upto 159°C due to seperation of S_8 unit. After 159°C on further increase in temp. due to S_8 unit broken, & open chain

सूरज पर रात में जाओ क्यूकि ठण्डा होगा 17/Oct/2014

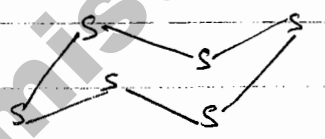
Pappu thinks such.

zig zag str. which forms polymeric str. finally, after 172°C viscocity decreases due to breaking of linear chain into descreate S_4, S_8 etc units. In vapour phase 'S' exist in S_2



Catena 'S' or plastic sulfur ⇒ chain like

Engel's sulfur:- S_6

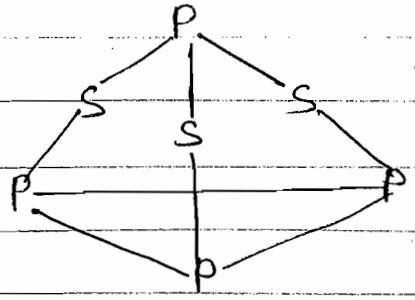


$\xleftarrow{-2HCl}$ $S_2Cl_2 + H_2S_4$

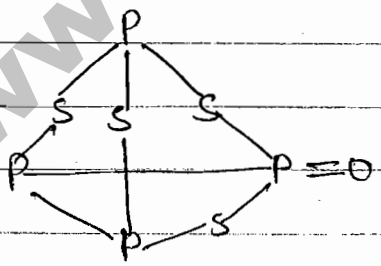
S_{12} has max. melting point

~~Imp~~

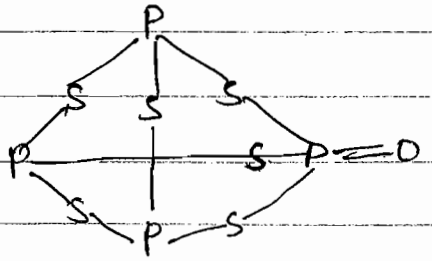
'P'-'S' compounds:- P_4S_3



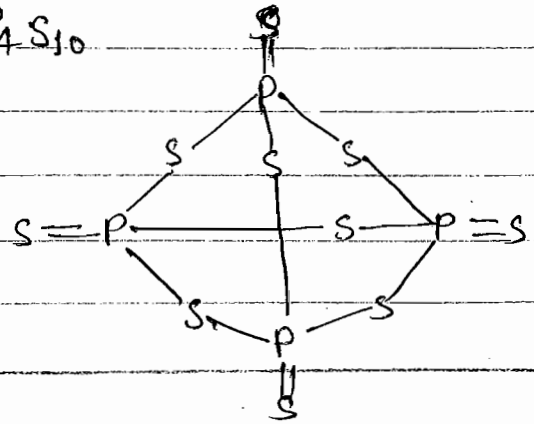
P_4S_5



P_4S_7



P_4S_{10}

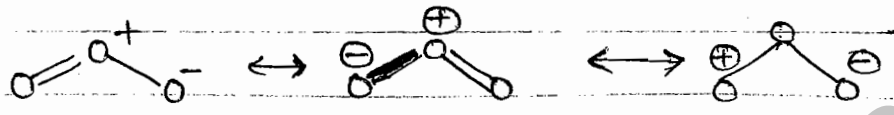


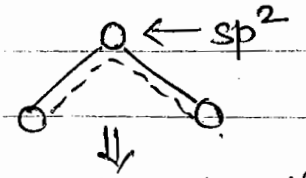
Force of gravity on equator is lowest i.e. why people living on equator are tall & black.

$KClO_3 + P_4S_3 + Red\ P \Rightarrow$ Match Box.

Allotropes of Oxygen:- O_2 & O_3

$O_2 + O_2 = O_4$

O_3 



3C, 4e bonding ⓐ Banana bonding

Formation O_3 is endothermic process, takes place via $h\nu$ radiation.

$\Rightarrow$ $O_2 \xrightarrow{h\nu} \dot{O} + \dot{O}$

$\dot{O} + O_2 \longrightarrow O_3$

$2O_3 \longrightarrow 3O_2$

Imp.

Wave length of $O_3 \Rightarrow$ 255 nm.

O_3 layer is present in stratosphere. It is formed in upper atm. due to $\dot{O} + O_2 \xrightarrow{h\nu} O_3$. O_3 absorbes in 255 nm strongly due to which its protective nature results lowering of temp. (18°C) ⇐ Average temp. O_3 layer depletion was discoved by farmann. Nobel prize to Tutzen in 1995.

$O_3 \Rightarrow$ Diamagnetic $O_2 \Rightarrow$ Paramagnetic

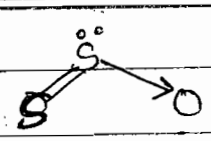
Blue colour

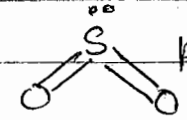
Oxides of Sulfur:- S_2O, SO, SO_2

Sulfur suboxide

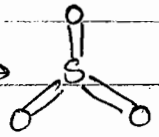
Size of all isotopes are always similar (e^- & proton equal)

$\Rightarrow$ $H = D = T$ $\quad$ $^{35}Cl = {}^{37}Cl$

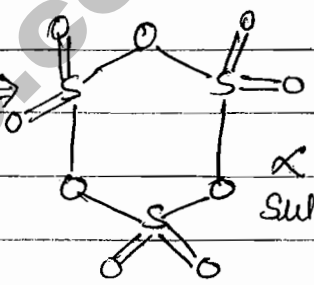




polar, $S{=}O$ Highly unstable

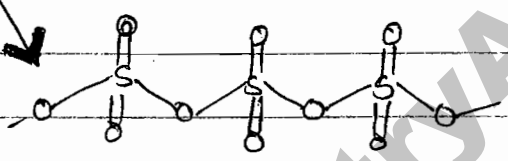
SO_3 —gas→  non polar ($\mu = 0$) Lewis acid.

SO_3 —Solid→

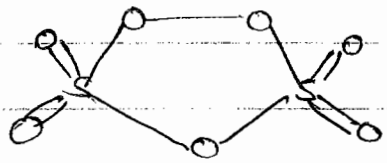
$\alpha (SO_3)_n \Rightarrow S_3O_9$ 

α Sulfur

$\beta (SO_3)_n$

$\gamma (SO_3)_n$ 

$\Rightarrow S_2O$, SO, S_2O_3, SO_2, S_2O_4, S_2O_5, SO_3, S_2O_7 → Acidity ↑

S_2O_7 

Hydrogen Compounds :-

H_2O	Size ↑
H_2S	T.S. ↑
H_2Se	Reducing power ↑
H_2Te ↓	acidity ↑

Q. H_2S is more st. acidic than H_2O because.

a) H—S bond energy is less. True

b) C.B. $\bar{S}H$ is more stable False

* H_2O $\quad$ D_2O $\quad$ T_2O

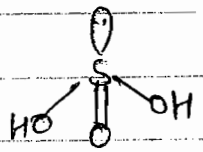
mass ↑ $\quad$ bp ↑

If Oxidation state is more than val. e^- then peroxide bond will be surely +nt.

D_2O is not good solvent although it has greater dielectric const than H_2O, because it is highly viscos. viscosity is due to deuterium bonding (just like H.B.). D_2O is used in reactors to slow down the speed of Neutron.

Oxo Acid of 'S' Most common are sulfurous & sulfuric series.

H_2SO_3

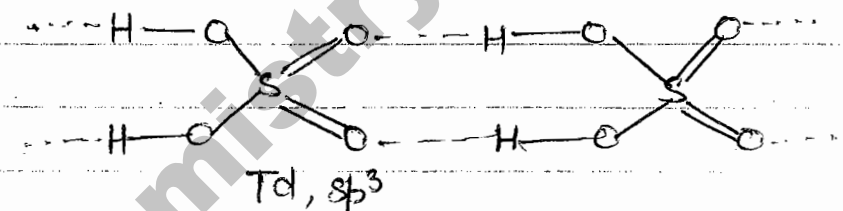


Geo - Td

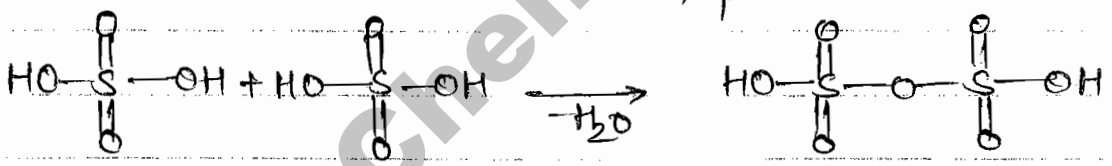
Shape - TBP

H_2SO_4

King of chemicals, oil of green vitriol, Rectified oil of vitriol, Green vitriol.



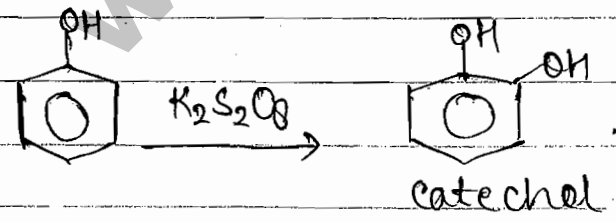
Td, sp^3



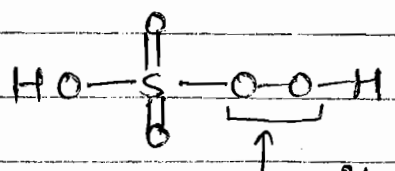
oleum ($H_2S_2O_7$)

Peracids:- H_2SO_5 (caro acid) Permono sulfuric acid.

(Marshall acid) $H_2S_2O_8$ Per disulfuric acid.



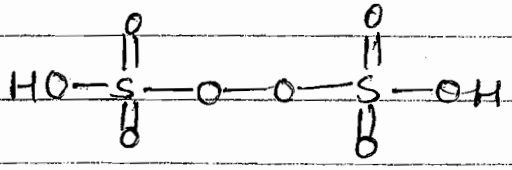
catechol + Quinol.



peroxide 'O' -1 O.No.

O.S. of S' $\Rightarrow +2-2-6+x=0$

$x = +6$



$+2-2+2x-12=0$

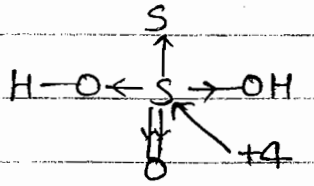
$x = +6$

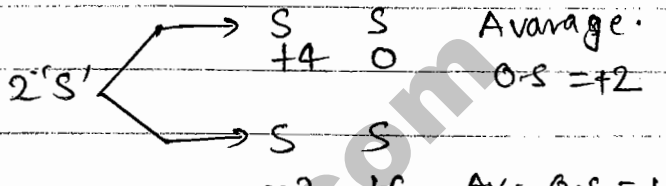
Most Imp ⇒ If 'O' atoms are odd then S–S bond –nt.
If 'O' " " even then S–S " +nt

Hypo oxo acid :- $H_2S_2O_3$ ⇒ Thio sulfuric acid.

$+2 + x - 6 = 0$

$x = +2$



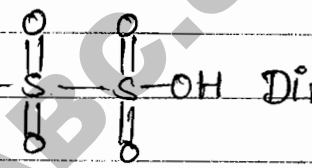


M.Imp.

* HO–S–S–OH Dithionous acid

'S'–'S' bonding ?

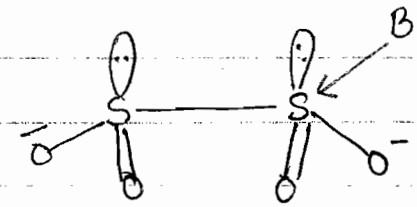
4 'O' (even)



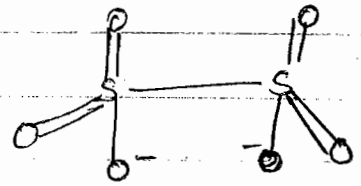
Dithionic acid.

6 'O' (even)

*



Eclipsed
non planar.

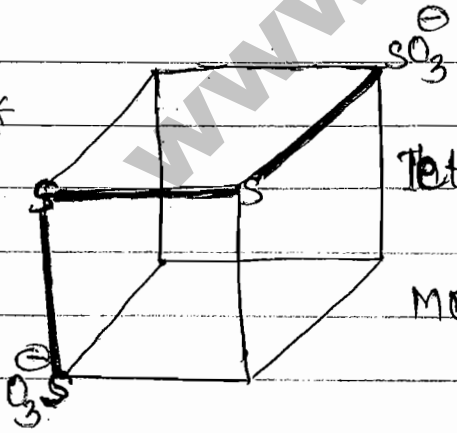


Eclipsed

⇒ $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + NaI$

Sod. thiosulphate — Sod. tetra thionate

*



Tetra thionate

Max. 'S' in plane = 3

HALOGENs

Halos + gen
Sea Salt

F_2	Gas	Diatomic
Cl_2	Gas	
Br_2	Liq.	
I_2	solid	
At	← Monoatomic metallic	

Imp

* Bond Dissociation Energy $Cl_2 > Br_2 > F_2 > I_2$

B.D.E of $H_2 > Cl_2$ 

Size & lp-lp. effect

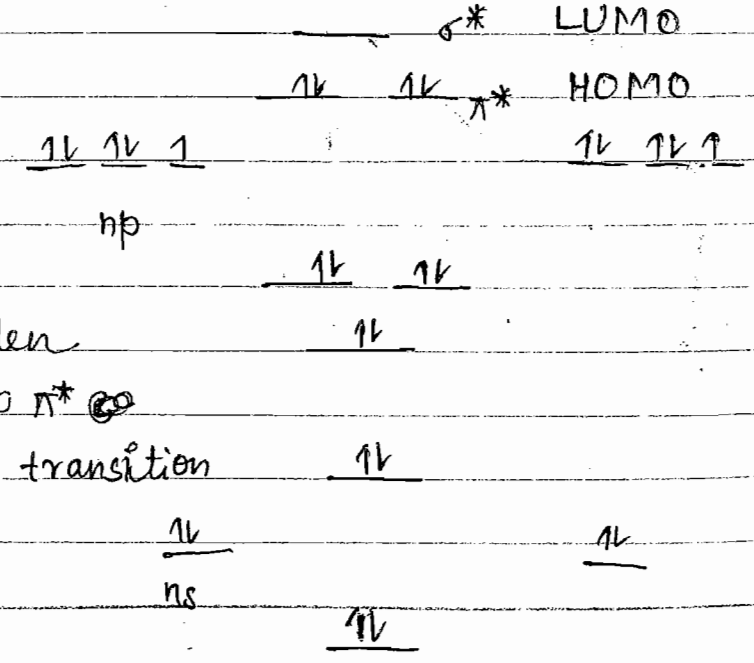
I.E. $F > H > Cl > Br > I$

Although the I.E. of H is more than that of Cl, Br, I but the formation of $H^{\oplus}$ is compensated by H's high hydration energy in sol^{n} & high lattice 'E' in solid state but H.E. & L.E. of Cl^{-}, Br^{-}, I^{-} are low don't compensate.

M. Imp GATE NET

$\pi^* \longrightarrow \sigma^*$
$g \qquad u$

This transition is responsible for colour of Halogens.
Even this transition is forbbiden ($g \rightarrow u$) but energy gap b/w π^* & σ^* is very less i.e. why transition take place.



18/10/2014

Iodine vapour. $\pi^* \longrightarrow \sigma^*$ transition $\Rightarrow$ violet

Iodine show metallic cluster.

Solubility :- Lewis Acid Base character :-

$I_2 + H_2O \longrightarrow$ Less soluble

$I_2 + KI \longrightarrow$ More soluble

$KI_3 \equiv K^{\oplus} I_3^{\ominus}$

$I^{\ominus}$ → I_2 (e^- donation in σ^* LUMO of I_2) $\longrightarrow$ $I_3^{\ominus}$

I_2 : B.O. = 1

$I_3^{\ominus}$: B.O. < 1

$\bar{\nu}_{I-I}$ $\quad I_2 > I_3^{\ominus}$

$\Rightarrow F^{\ominus} + F_2 \longrightarrow F_3^{\ominus}$

$Cl^- + Cl_2 \longrightarrow Cl_3^{\ominus}$

$Br^- + Br_2 \longrightarrow Br_3^{\ominus}$

$I^{\ominus} + I_2 \longrightarrow I_3^{\ominus}$

T.S. ↑ ↓

$Li^{\oplus}\ I_3^{\ominus}$

$Na^{\oplus}\ I_3^{\ominus}$

$K^{\oplus}\ I_3^{\ominus}$

$Rb^{\oplus}\ I_3^{\ominus}$

$Cs^{\oplus}\ I_3^{\ominus}$

T.S. ↑ ↓

$\Rightarrow$ for polyhalide general $Na^{\oplus} < K^{\oplus} < NH_4^{\oplus} < Rb^{\oplus} < Cs^{\oplus}$ order

① I_2 - Cyclohexane, solvent ② I_2 - Benzene solvent ③ I_2 - Et_2O solvent.

* I_2 forms more easily complex with solvent having more donating ability.

* donating ability of solvent: Et_2O > Benzene > C_6H_{12}

⇒ more donation of e^- in π^* (LUMO) of I_2, less will be bond order.

① < ② < ③

μ ↑, complex formation ↑

B.O. ↓, Bond length ↑.

Interhalogen Compounds (I.H.C.)

The binary comp. of halogens are called I.H.C. No neutral ternery, quartarnary comp: are stable. In IHC central atom never be F & surrounding atom never be I. Central halogen is having O.S. +1, +3, +5, +7. & sarrounding halogen have O.S. −1.

AB	AB_3	AB_5	AB_7
ClF	ClF_3	ClF_5 } Gas	IF_7 Gas
BrF	BrF_3	BrF_5	
ICl	IF_5	IF_5	
IF	ICl_5		
BrCl	IBr_3		

Preparation: $I_2 + Cl_2 \longrightarrow 2ICl$

$Cl_2 + F_2 \xrightarrow{T_1} ClF$ $\qquad T_1 < T_2 < T_3$

$\xrightarrow{T_2} ClF_3$

$\xrightarrow{T_3} ClF_5$

Properties: ① As non aqueous solvent

② Fluorinating agent

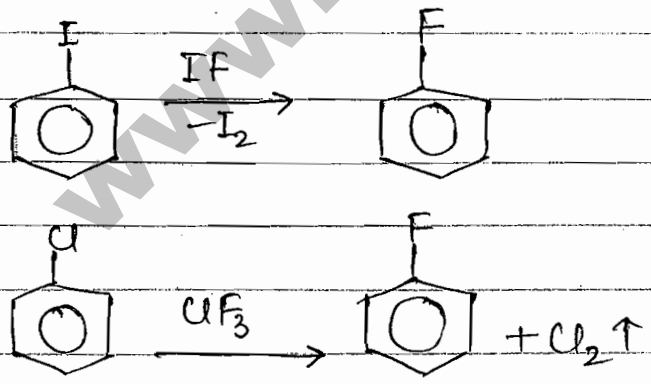
$KCl \xrightarrow{H_2O} K^{\oplus} + Cl^{\ominus}$

No any ion resembling with ion of $H_2O (H^{\oplus} \& OH^{\ominus})$ so KCl in water is salt.

$KCl \xrightarrow{liq.\ ICl} K^{\oplus} + Cl^{\ominus}$

↳ Anion resembling with ion of ICl, $(I^{\oplus}\ Cl^{\ominus})$ so KCl in ICl is base.

⇒ **Fluorination**



Enrichment of Urenium

$UO_2 \xrightarrow{BrF_3} UF_4\uparrow$

$\xrightarrow{ClF_3} UF_6\uparrow$

} source of urenium

Rxn. with metal Halide

$KCl + ICl \longrightarrow K^{\oplus} ICl_2^{\ominus}$

$KBr + ICl \longrightarrow K^{\oplus}[ICl Br]^{\ominus}$ $\xrightarrow{\Delta}$ $KCl + IBr$ ✓ More LE of KCl than KBr & KI

$\xrightarrow{\Delta}$ $KBr + ICl$ ✗

$\xrightarrow{\Delta}$ $KI + ClBr$ ✗

$KCl + ClF_3 \longrightarrow K^{\oplus}[Cl_2F_3]^{\ominus}$

$CsCl + ICl \longrightarrow Cs^{\oplus}[ICl_2]^{\ominus}$ $\xrightarrow{\Delta}$ $CsI + Cl_2$ ✓

$\xrightarrow{\Delta}$ $CsCl + ICl$ ✗

Addⁿ Rxn.

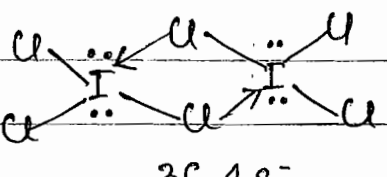
$CH_3-CH=CH_2 + I^{\oplus}Cl^{\ominus} \longrightarrow CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-I$

Iodine Value:-

ICl is used in determining the iodine no. of fat/oil. ICl ⇒ Wij's Reagent.

Str.

ICl_3 exist in dimer form I_2Cl_6



3C-4e⁻ bond

Stability :- Planar str. (2D)

The stability of interhalogens depends upon-

① Electronegativity diff. ⇒ When same type of IHC consider.

② Size of C. Atom & surrounding atom.

③ for diff. type class having same halogens → More the no.

of surrounding atoms, more will be stability due to high +ve charge/O.S. on central atom NET: 2012 D

$IF_7 > IF_5 > IF_3$

← Stability ↑

AB_3	ClF_3	BrF_3	IF_3
$\chi_A \sim \chi_B$	1	1.2	1.5

→ Stability ↑

ClF BrF IF, BCl

Dipole moment: Check two points :- ① Str. ② Electronegativity.

$ClF_3 < BrF_3 < IF_3$

$\chi_A \sim \chi_B$	1	1.2	1.5

→ Polarity ↑ μ ↑

Reactivity:

F_2 is the only halogen which is more reactive than interhalogen comp, rest Cl_2, Br_2, I_2 are less reactive than interhalogen comp.

⇒ F—F is more reactive due to lp.-lp. repulsion.

⇒ ClF_5 is at second position in reactivity.

⇒ for diff. kinds of IHC reactivity decreases with the decreament of electroneg. of C. Atom.

⇒ Sulfur fluoride except SF_6 more reactive than 15th gp. th Fluoride.

⇒ Penta Fluoride of As & Sb are more reactive than tri fluoride due to unstable T.B.P. str.

Reacctivity order.

? $F_2 > ClF_5 > ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5$

Oxoacid :- acidity ↓ due to ↓ electroneg. of C.A. →

$\overset{-1}{H}OF$	$H\overset{+1}{O}Cl$	$H\overset{+1}{O}Br$	$H\overset{+1}{O}I$	acidity ↑ due to ↑ stability of C.B.
	$HClO_2$	$HBrO_2$	HIO_2	
	$HClO_3$	$HBrO_3$	HIO_3	
	$HClO_4$	$HBrO_4$	HIO_3	

$HOF \longrightarrow \overset{\oplus}{H}O + \overset{\ominus}{F}$ Hydroxy Fluoride

$HOCl \longrightarrow \overset{\oplus}{H} + \overset{\ominus}{O}Cl$

$HClO_2$ chlorous acid

$HClO_3$ Chloric acid

$HClO_4$ Per " "

Imp.

Oxidising Power :-

* Fluorine is strongest O. agent.
* Perxenate ion is at II position
* the oxidising power of anions of oxoacids of halogens decreases with the increasing oxidn state for same C.A.

$Cl_2 \cong ClO^- > ClO_2^- > ClO_3^-$

$Br_2 \backsimeq BrO^- > BrO_2^- > BrO_3^-$

Conc. HF is more acidic than dil. HF. except HF all other acids are " " in dil. form.

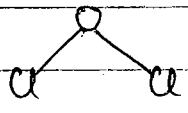
The oxidising power of perhalogenate depends upon redox potential where BrO_4^- shows abnormal character of high oxidising power.

Most Imp. $\boxed{F_2 > BrO_4^- > IO_4^- > ClO_4^-}$ 2014 D

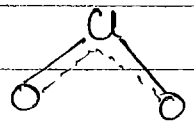
Oxides:- ⇒ I_2 forms max. no. of oxides.

⇒ F_2 " only 2 comp. OF_2 & O_2F_2.

⇒ Cl_2 forms Cl_2O, Cl_2O_3, ClO_2, Cl_2O_5, Cl_2O_7



Diamag



odde⁻ spp. ⇒ Paramagnetic

⇓

don't form dimer because single e⁻ shows resonance.

⇒ I_2 forms. I_2O_4, I_4O_9, I_2O_5

$I^{\oplus}O\ I^{\ominus}O_3$ ← I_2O_4 ; I_4O_9 → $I^{+3}(IO_3)_3^{\ominus}$

Iodine(III) Iodate(V)

Hydra Acids:-

Anhydrous state

$HF + HF \rightleftharpoons H^{\oplus} + HF_2^{\ominus}$

HF
HCl
HBr
HI

acidity ↑ (Hydrous medm)

HF in aq. medm. is weak acid but in anhydrous condn. ion pair doesn't form, ~~not~~ becoz $HF_2^{\oplus}$ form which is more stable

HF exist in dimeric form $\Rightarrow H_2F_2$ because —

$$2HF \rightleftharpoons H^{\oplus} + HF_2^{\ominus}$$

$HF_2^{\ominus}$ ← Highly stable

2011, 13 Imp.

* $2HF + HNO_3 \longrightarrow HF_2^{\ominus} + H_2NO_3^{\oplus}$
(HF: acid, HNO_3: Base)

$2HF + H_2SO_4 \longrightarrow HF_2^{\ominus} + H_3SO_4^{\oplus}$

$2HF + CH_3COOH \longrightarrow HF_2^{\ominus} + CH_3COOH_2^{\oplus}$

M. Imp.

$HF + HClO_4 \longrightarrow ClO_4^{\ominus} + H_2F^{\oplus}$
(HF: Base, $HClO_4$: Acid.)

Normal miniral acids HNO_3, H_3PO_4, HBr; which behave as acid ($H^{\oplus}$ donar) in water. Behave like base in liq. HF. Only one Acid ($HClO_4$) maitain it's char- which is acid in liq. HF.

⇒ HF used in Itching of Glass (designing of Glass)

⇒ $SiF_4 + HF \longrightarrow H_2[SiF_6]$

PERIODIC TABLE

Law of Triad:

The properties of midde element are the intermediate of Ist and IIrd element.

Law is valid only for ~~the~~ group No. 18 and the elements of Fe, Co, Ni, family.

Ar
Kr
Xe

$$B.P. \text{ of } Kr = \frac{Ar + Xe}{2}$$

Na & Mg Bridge Elements

New Mendeleef Periodic table:-

Periodic Law:- The properties of element are periodic function of their atomic numbers i.e. when elements are arranged in increasing order of their atomic no., after definite interval ↵ elements of similar property are repeated. this repetition is called. periodicity of element.

Typical Elements:
element of II & III period are called typical elements or representative element becoz they shows the characteristic properties of their respective gps

Elements of III period: Na, Mg are called bridge element. becoz they shows the similarities with the two subgps of their gp.

Diagonal relation ship :- Li, Be B

Modern Periodic Table (or) Long form of P.T. (or)

Bohr's P.T. (or) Expanded P.T.

P.T. is sylidrical not planar

Smallest atom H
Biggest " Fr (or) Cs
Highest I.E. He
Lowest " Fr, Cs

Most χ(F
least χ(He
Highest electron Affinity Cl
Lowest " " Au (Gold) or Noble Gas
Liq. Metal Hg, Ga, Cs
Liq. Non " Br
Grasious nometal — Cl_2, F_2, O_2, N_2
Noble gases are neither metal nor non metal.
Highest density. Ir. 22.61 gm/cc
or Os 22.58 " "
Highest m.p. 'C' then W
Elements after at no. 92 are man made
No. of Natural element = 91
Tc is also man made
Twince element Zr, Hf & Nb, Ta, & Mo, W
coinage metal Au, Cu, Ag
Most poisionous ⟶ Pu
Max O.S. ⟶ +9 by Pu
+8 by Xe, Os, Ru
Most costly element ⟶ Urenium.
Wonder element ⟶ Ti
Future " ⟶ Ti
Duckbill platipus element Tl ← Connective link.

0	1	2	3	4	5	6	7
nill	Un	bi	Tri	quad	pent	Hex	Sept

⇒ 'H' forms more comp. than other elements.

Talphate is not in P.T.

Lr (Y) Lw Both symbol.

~~Element after~~

at. No. 83 (Bi) are radioactive.

Atomic Size

It is distance b/w Nucleus & most loosly bonded e⁻ of last shell. Atomic radius is determined by the nature of element, It is of many type:-

Co-valent radius:-

Homodiatomic

H_2, Cl_2

$r_H = \frac{d}{2}$

Heterodiatomic

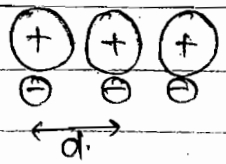
H——Cl

$d_{HCl} \neq r_H + r_{Cl}$

Radius determined by Stevenson-Shoemaker eqn.

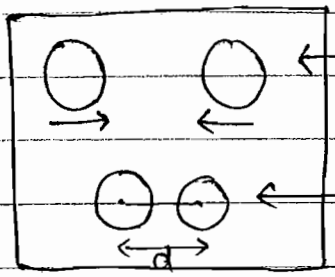
$d_{HCl} = r_H + r_{Cl} - 0.09 (\chi_H \sim \chi_{Cl})$

Metallic Radius:-



$r_M = \frac{d}{2}$

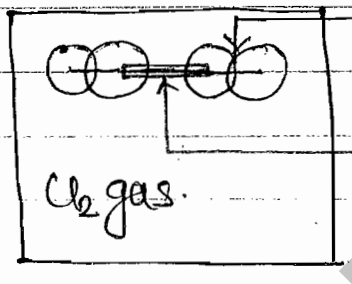
V. Wall Radius:- Non-bonded System.



At the time of collision (minimum distance V.W.R = $\frac{\sigma}{2}$ ← in place of d.

Imp.

VWR > Metallic Radius > Covalent Radius



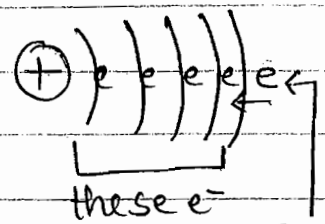
Ionic Radius:- anion (Larger size than parent element)
cation (Small size than parent element)

Ex. $Cl^{+7} < Cl^{+} < Cl < Cl^{-} < Cl^{--}$

⇒ All the elements has all type of radius.

Alkali metals in gaseous form exist in dimer form eg. Na_2, K_2 ---

Shielding Effect:-



$$Z_{eff} = Z - S$$

S ↑ Shielding const.

Slater Rule: for calculation screening const(S):-

Steps-

1) Write the e⁻ ic configuration in following manner-

(1s) (2s 2p) (3s 3p) (3d) (4s 4p) (4d) (4f) - —

2) Calculation of 'S' two types -

i) For ns & np e⁻s

a) Contribution in 'S' by n ēs = 0.35

b) " " " " (n-1)ēs = 0.85

c) " " " " (n-2)(n-3); ..... = 1

ii) For nd & nf e⁻s

a) Contribution in 'S' by nd/nf e⁻s = 0.35

b) " " " " rest e⁻s = 1

3) if e⁻ is +nt only in 1s then contribution = 0.30

④ If the screening const is to be determined at periphery of atom, then include all electrons.
If e^- inside periphery then include one less e^-.

Ex. $\boxed{Z_{eff} = Z - S}$

$K(19) = (1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(4s^1)$

n-3	n-2	n-1	n
1	1	0.85	0.35

$S = [0 \times 0.35] + (8 \times 0.85) + (10 \times 1)$

$Z_{eff} = Z - S$

$= 19 - S \Rightarrow 19 - 16.8 = 2.2$

↳ At No of K

Ex. $Mg(12) = (1s^2)(2s^2 2p^6)(3s^2)$

1	0.85	.35

$S = (1 \times 0.35) + (8 \times 0.85) + 1 \times 2$

$= 9.15$

$Z_{eff} = Z - S$

$= 12 - S$

$= 12 - 9.15 = 2.85$

If 19th e^- of K in d orb. then

$K = (1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^1)$

			n
1	1	1	0.35

$Z_{eff} = 19 - (0 \times 0.35) + (18 \times 1)$

$= 19 - 18 = 1$

Z_{eff} is less (1) if e^- enters in 3d orb. so less interaction of e^- with Nucleus i.e. why last e^- enters in 4s rather than 3d.

Ex.

Fe = $(1s^2)$ $(2s^2 2p^6)$ $(3s^2 3p^6)$ $(3d^6)$ $(4s^2)$

n-2	n-2	n-1	n-1	n
1	1		0.85	0.35

For 4s $Z_{eff} = 26 - [(1 \times 0.35) + (14 \times 0.85) + (10 \times 1)]$

$= 26 - 22.25$

$= 3.75$

for 3d e^-

$Z_{eff} = 26 - [(5 \times 0.35) + (18 \times 1)]$

$= 26 - 19.75$

$= 6.25$

$\Rightarrow$ e^- preffers the orb which has lower value of $(n+l)$ Klechkowasky Rule

Ex. 4s 3d

$4+0 = 4$ ✓ $3+2 = 5$ ✗

19/10/014

Zeff.

H (1)

Li	Be	H	F	He
1.3	1.95	01	5.2	1.7
Na	Mg			
2.2	2.85			
K				
2.2				
Rb				
2.2				

Increasing ↓

const.

More Zeff. i.e. why highly bounded e⁻

Zeff ↑

Zeff ↑

Zeff (same after 3 elements).

Imp Calculate Zeff. on periphery. ⇒ include all e⁻ (means contribution of all e⁻).

Nucleus] ns np nd nf

← Penetration effect ↑

Diffusion ↑ →

Shielding effect ↓ →

S, p ⇒ nearly same & max. S.E.

f ⇒ Highly diffused almost zero S.E.

d → d^1, d^2, d^3, d^4, d^5 ⇒ Almost neglegible S.E.

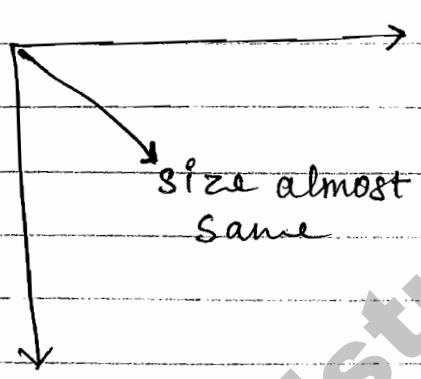
d → $d^6 \simeq d^7 \simeq d^8 \simeq d^9$ d^{10} Max. S.E.

size $\propto$ S.E.

$I.E. \propto \frac{1}{S.E.}$

Size.

In general.



Size $B > C > N > O > F > Ne$ (C.V.R. | V.W.R.)

Vander wall Radius. always bigger than other radius.

Size $B > C > N > O > F > Ne$ (C.V.R.)

Size $Al > Si > P > S > Cl$

Sc Ti V Cr Mn Fe Co Ni Cu Zn.

~~d^1~~ ~~d^2~~ d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

d^1 — d^5 S.E. negligible

d-pairing of e^- take place

d^{10} S.E max.

Lanthanide Slow decrament ⇒ Contraction.

Lanthanoid Contraction :-

⇓

Tendency to form complex with negative ion.

Lanthanoid & Actanoid ⇒ Group no. 3.
Longest group ⇒ 3
Longest period ⇒ 6th.

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

The slow and steady decrease in the size from Ln to Lu is called Ln contraction.

Electronegativity of Ln almost similar.

P.N.											
5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
6	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		

Ln (58 – 71)

Post lanthanoid element

⇓

more density due to Ln contraction

⇓

Ti < Zr = Hf More m.p.

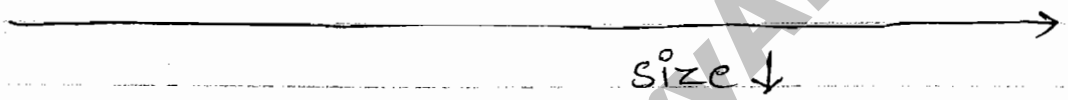
V < Nb = Ta

The properties of post Ln element get get change due to Ln contraction. Size of 5d series element get similar to 4d series element due to Ln contraction

Imp.

Size Isoelectronic species:-

	N^{---}	O^{--}	F^{-}	Na^{+}	Mg^{++}	Al^{+++}
p	7	8	9	11	12	13
$e^{-}s$	10	10	10	10	10	10



size ↓

Isoelectronic Ionisation Energy / Ionisation Potential

(or) Ionisation Enthalpy ($\Delta_i H$) :-

The amount of energy needed to release the most loosely bonded e^- from the last shell of an isolated gaseous atom/ molecule, is called I.E. $M \xrightarrow{\text{I.E.}} M^+ + e^-$

the term I.E is not a good term, as it represents need of Energy to release the e^- at 0K, which can't be possible.

Therefore in actual practice one should study the term Ionisation enthalpy. this includes heat capacity also & it determind at 298K by Born haber cycle.

$U_{0K} \backsim \Delta H_{298} \backsim 6.2\ KJ/mol$

as this diff is low, therefore in studies I.E & ΔH are used simultaneously.

For any element the total no. of I.E. will be equal to the no. of e^- i.e. 11 I.E are possible & are known for Na. I.P. is the term of physics and is represents the energy needed to release 1 e^- from an isolated single atom

Factors Affecting I.E.

I.E $\propto$ Nuclear charge

I.E $\propto$ Zeff

I.E $\propto \frac{1}{\text{Size}}$

I.E $\propto \frac{1}{\text{S.E.}}$

* Stability of configuration. Half filled or full filled more stable $\Rightarrow$ High I.E.

* Penetration effect

I.E. $ns > np > nd > nf$

apply for two adjacent atoms.

* Nature of orb. $IE_{BMO} > {}^{I.E.}_{ABMO}$

Successive I.E. :-

$$M_g \xrightarrow[-e]{I_1} M^+_g \xrightarrow[-e]{I_2} M^{++} \xrightarrow[-e]{I_3} \cdots\cdots$$

$$Al \xrightarrow[I_1]{-e^-} Al^+ \xrightarrow[I_2]{-e} Al^{++} \xrightarrow[I_3]{e^-} Al^{+++}$$

$I_1 < I_2 < I_3 < \cdots\cdots$

In General,

Gradation.

→ size ↓
I.E. ↑

↘ size almost same
Zeff ↑, I.E. ↑

↓ size ↑
I.E. ↓

penetration effect — Stable — full filled

Li	Be	B	C	N	O	F	Ne
$2s^1$	$2s^2$	$2s^2$ $2p^1$	$2s^2$ $2p^2$	$2s^2$ $2p^3$	$2s^2$ $2p^4$	$2s^2$ $2p^5$	$2s^2$ $2p^6$

$I_1 \Rightarrow$ Li < B < Be < C < O < N < F < Ne

Li^+	Be^+	B^+	C^+	N^+	O^+	F^+	Ne^+
$2s^0$	$2s^1$	$2s^2$ $2p^0$	$2s^2$ $2p^1$	$2s^2$ $2p^2$	$2s^2$ $2p^3$	$2s^2$ $2p^4$	$2s^2$ $2p^5$

→ size ↓

$I_2 \Rightarrow Be^+ < Li^+ < C^+ < B^+ < N^+ < F^+ < O^+ < Ne^+$

Li^{++}	Be^{2+}	B^{++}	C^{++}	N^{++}	O^{++}	F^{++}	Ne^{++}
$1s^1$	$1s^2$	$2s^1$	$2s^2$	$2s^2$ $2p^1$	$2s^2$ $2p^2$	$2s^2$ $2p^3$	$2s^2$ $2p^4$

→ size ↓

$I_3 \Rightarrow Li^{++} < B^{++} < Be^{++} < N^{++} < C^{++} < O^{++} < Ne^{++} < F^{++}$

I II

N O Na Mg

$2s^2$ $2s^2$ $2p^6\ 3s^1$ $2p^6\ 3s^2$

$2p^3$ $2p^4$ ↓ $I_1 < I_1$ ↓

Stable Na^+ Mg^+

$I_1 > I_1$ $2p^6$ $2p^6\ 3s^1$

$I_2 > I_2$

Na^{++} Mg^{2+}

I.E. Hf > Ti > Zr $2p^5$ $I_3 < I_3$ $2p^6$ stable

↑ ↓ ↓

small size ⇒ more Zeff. Na^{3+} Mg^{3+}

due to Ln contraction. $2p^4$ $I_4 < I_4$ $2p^5$

↓ ↓

Na^{+4} Mg^{+4}

I_1 Ca < Ga $2p^3$ $I_5 > I_5$ $2p^4$

↓ ↓

I_1 K < Ca < Ga. Na^{+5} Mg^{+5}

$2p^2$ $I_6 < I_6$ $2p^3$

Zn > Ga

$3d^{10}4s^2$ $3d^{10}, 4s^2, 4p^1$

Cd > In

Hg > Tl

⇒ Ca Cu

20 29

$4s^2$ $4s^1 3d^{10}$

$I_1 < I_1$

Ca^+ Cu^+

$4s^1$ $3d^{10}$

$I_2 < I_2$

Determination of I.E. for Hydrogen Like System:-

I.E. of H = 13.6 ev/atm.

for 'H' like system / one e^- system Li^{++}, Be^{+3}, Na^{+10}

$$E = \frac{13.6\ Z^2}{n^2}$$

Li^{2+} = IE ?

$$E = \frac{13.6 \times 3^2}{1^2} = 9 \times 13.6$$

Imp.

Oxidation state V/S I.E.I-

If the diff. in I.E. two successive I.E. is less than 16 KJ/mole then higher O.S. will be more stable and if the diff greater than 16. then lower O.S. is more stable.

$$A \xrightarrow[I_1]{8} A^+ \xrightarrow[I_2]{12} A^{++} \xrightarrow[I_3]{120} A^{3+}$$

O.S. = +1 O.S. = +2

$A^+ \longrightarrow A^{++}$

8 ∿ 12

= 4

$A^+ < A^{++}$

$A^{++} \longrightarrow A^{+++}$

12 ∿ 120

= 108

$A^{++} > A^{+++}$

$\Rightarrow$ Ni^{++} < Pt^{++}

$(I_1 + I_2)$ $(I_1 + I_2)$

Only 17 elements are non metal in Periodic table
He Ne Ar have highest I.E. in P.T.

$H_2[\overset{IV}{Pt}F_6]$ (or) $K_2[\overset{IV}{Pt}F_6]$ exists $K_2[\overset{IV}{Ni}F_6]$ doesn't exist

$Al^+ \xrightarrow{I_1} Al^{2+} \xrightarrow{I_2} Al^{3+} \xrightarrow{I_3} Al^{4+}$

$I_1 < I_2 < I_3 << I_4$
Jump.

Electron Affinity (or) Electron Gain Enthalpy:-

Electron affinity is the hypothetical ideal word but used still now. The energy release when e^- is added in isolated neutral gaseous atom, in their ground state, is called E.A.

The enthalpy change at 298 K when 1 e^- is donated to an isolated neutral gaseous atom in it's G.S. is called electron gain enthalpy ($\Delta_{eg}H$)

Sign Convention:-

$EA = +10$

$\Delta_{eg}H = -10$

Ans. only for NET, GATE.

Q. The E.A. of 'O' is
a) -10
b) +10

Q. The E.G.E. of 'O' is -
a) -10
b) +10

Q. The E.A. & E.G.E. of 'O' are.
a) -10, +10, b) +10, -10 c) -10, -10 d) +10, +10

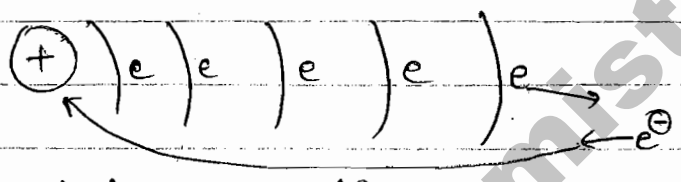
26/10/2014

Factors affecting E.A.

1) $EA \propto \frac{1}{size}$

2) $EA \propto Z_{eff}$

3) Stability of configuration: for stable conf: the intake of e^- therefore they may either having +ve E.A. or having zero E.A. Ex. 15th gp element like 'N' 2nd gp. element like Be, Mg they may have +ve EA which are considered as zero.



Nuclear attraction (Exothermic) e^--e^- repulsion (Endothermic)

1) e^--e^- > NA endo
2) e^--e^- < NA Exo

(4) e^--e^- Repulsion. ⇒ for small size e^- density high e^--e^- repulsion high ⇒ E.A. decreases.

5) Penetration Effect.

E.A. ns > np > nd > nf

Ex. Na > Mg

Na: $ns^1 \leftarrow e^\ominus$ Mg: $ns^2, np^\circ \leftarrow e^\ominus$

E.A. ⇒ Most abnormal property of P.T.

ns^1 ns^2

Li < be Size factor dominant

11	12	13	
Cu	Zn	Ga	E.A. 11 > 13 gp.
Ag	Cd	In	
Au	Hg	Tl	
$d^{10}s^1$	$d^{10}s^2p^0$	ns^2np^1	

* E.A. of halogens highest in periodic table

Cl > F > Br > I

Smallest ⇒ high e^- density, less E.A. than Cl

* 14th gp Si > C > Ge > Sn > Pb

* 16th gp. S > Se > Te > O

* 13th gp. Al > Ga > In > B

* N P As Sb

N: E.A. +ve; P, As, Sb: E.A. -ve

Successive Electron Affinity:-

$O \xrightarrow{e^-} O^{\ominus} \xrightarrow{e^-} O^{2-}$

E_1 E_2

E_2, E_3 ---- with be +ve

$\chi_{-CF_3} > F$

Electronegativity (χ) :- It is the relative property. Hence not having fixed value

Scales of Electronegativity :-

1) Pauling Scale :- Based upon bond energy ; thermo-dynamical scale. Here χ of F, H has been fixed. $\chi_F = 4$ $\chi_H = 2.1$

$$(\chi_A \sim \chi_B) = 0.208\sqrt{\Delta}$$

Δ ↑ Extra Energy or resonance Energy.

$$\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

2) Mulliken Scale $\chi = \frac{I.P + EA}{2}$

The values at mulliken scale comes to be 2.8 times more than that at Pauling scale.

3) Allred-Rochow Scale :-

$$\chi = 0.744 + \frac{0.359\ Z_{eff.}}{r^2}$$

Factors affecting Electronegativity :-

$\chi \propto \frac{1}{\text{size}}$ $\chi \propto$ N.A. $\chi \propto$ +ve O.S.

$Fe^{2+} < Fe^{3+}$

$\chi \propto$ % s character

CH_3-CH_3	$CH_2=CH_2$	$CH\equiv CH$
sp^3	sp^2	sp
25%	33.3%	50%
$\chi_C \simeq 2.5$	$\chi_C \simeq 2.98$	$\chi_C \simeq 3.4$

Li	1
Be	1.3
B	2
S ≃ C ≃ I	2.5
N	3
O	3.5
F	4
H	2.1

χ T.M.E = 1.3 —— 2.1

χ Ln, Ac ≃ 1.3

Applications of Electronegativity :-

If the ~~electronegativity~~ % Ionic character is less than 25% the comp. will show colour spectra.

Ag_2S
AgBr
AgI
] coloured. due to LMCT

AgCl White colourless.

Pauling - 2 Nobel prize

for LMCT. Ionic character should be less than 25%

% I.C. → Dipole moment
% I.C. → Electronegativity method → Pauling Method.
Electronegativity method → Hanny-Smith

eqn. ⇒ % IC

$$\% \text{ I.C.} = 16(\chi_A \sim \chi_B) + 3.5(\chi_A - \chi_B)^2$$

Nature of Bond:-

⇒ Pauling method

$(\chi_A \sim \chi_B) = 1.7 \Rightarrow$ 50% ionic + 50% covalent.

" $> 1.7 \Rightarrow$ ionic bond.

" $< 1.7 \Rightarrow$ co-valent bond.

Exception H—F ⇒ 1.9 It should be ionic but it is co-valent bond.

⇒ Hanny-Smith.

$\chi_A \sim \chi_B = 2.1 \Rightarrow$ 50% ionic + 50% covalent.

$\chi_A \sim \chi_B > 2.1 \Rightarrow$ ionic bond.

$\chi_A \sim \chi_B < 2.1 \Rightarrow$ co-valent bond.